

(19) 日本国特許庁 (J P)

## (12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-298066

(43) 公開日 平成9年(1997)11月18日

(51) Int.Cl. <sup>8</sup>	識別記号	序内整理番号	F I	技術表示箇所
H 0 1 M	10/04		H 0 1 M 10/04	Z
	10/28		10/28	Z
	10/40		10/40	Z
	12/08		12/08	K

審査請求 未請求 請求項の数22 F D (全 18 頁)

(21) 出願番号 特願平9-65604

(22) 出願日 平成9年(1997)3月5日

(31) 優先権主張番号 特願平8-79079

(32) 優先日 平8(1996)3月5日

(33) 優先権主張国 日本 (J P)

(71) 出願人 000001007

キヤノン株式会社

東京都大田区下丸子3丁目30番2号

(72) 発明者 川上 純一郎

東京都大田区下丸子3丁目30番2号 キヤ  
ノン株式会社内

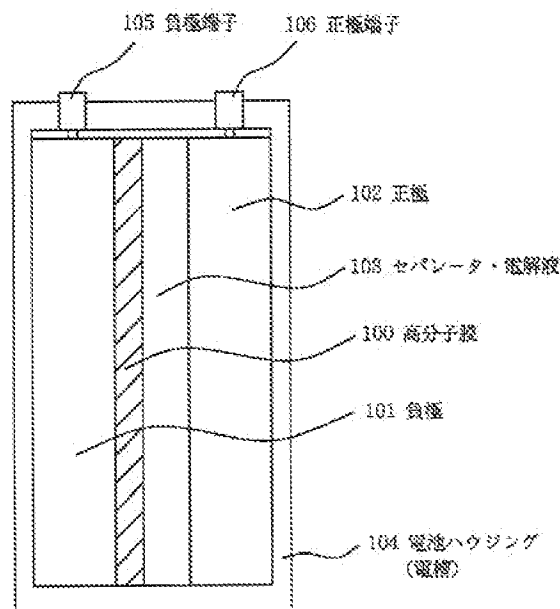
(74) 代理人 弁理士 渡辺 徳廣

(54) 【発明の名称】 二次電池

(57) 【要約】

【課題】 負極活物質としてリチウム又は亜鉛を用いた二次電池において、サイクル寿命を長くし、エネルギー密度を高める。

【解決手段】 負極101と、正極102と、該正極102及び負極101間において、電解質と、電池反応に関与するイオンが移動可能であり環境に応じて変動可能な孔径の連通孔を有する層100と、これらを収容する電池ハウジング104とを有する二次電池。



## 【特許請求の範囲】

【請求項1】 負極と、正極と、該正極及び負極間において、電解質と、電池反応に関与するイオンが移動可能であり環境に応じて変動可能な孔径の連通孔を有する層と、これらを収容する電池ハウジングとを有することを特徴とする二次電池。

【請求項2】 前記連通孔は、該連通孔周囲の領域に於ける電界強度及び／又は温度の変化に応じて孔径が変動する請求項1記載の二次電池。

【請求項3】 前記連通孔は、該連通孔周囲の領域に於ける電界強度の上昇及び／又は温度の上昇により孔径が小さくなる請求項2記載の二次電池。

【請求項4】 前記連通孔を有する層が、電界強度及び／又は温度の変化に応じて径が変動する細孔を有する高分子膜である請求項1記載の二次電池。

【請求項5】 前記高分子膜における細孔が、該細孔周囲の領域に於ける電界強度の上昇及び／又は温度の上昇により径が小さくなる請求項4記載の二次電池。

【請求項6】 前記高分子膜が高分子液晶からなる請求項4記載の二次電池。

【請求項7】 前記高分子液晶が、電界無印加下においては負極平面に対して垂直配向もしくは傾斜配向しており、電界強度の上昇及び／又は温度の上昇が生じた細孔の周辺においては、負極平面に対して実質的に平行又はランダムに配向する請求項6記載の二次電池。

【請求項8】 前記高分子液晶の誘電率異方性が負である請求項6記載の二次電池。

【請求項9】 前記高分子膜が高分子と液晶の複合体からなる請求項4記載の二次電池。

【請求項10】 前記高分子膜における液晶が、電界無印加下においては負極平面に対して垂直配向もしくは傾斜配向しており、電界強度の上昇及び／又は温度の上昇が生じた細孔の周辺においては、負極平面に対して実質的に平行又はランダムに配向する請求項9記載の二次電池。

【請求項11】 前記高分子膜における液晶の誘電率異方性が負である請求項9記載の二次電池。

【請求項12】 前記高分子膜が高分子ゲルからなる請求項4記載の二次電池。

【請求項13】 前記高分子ゲルが温度の上昇により20%以上体積膨張する請求項12記載の二次電池。

【請求項14】 セパレーターを有し、前記正極、セパレーター、前記高分子膜、前記負極がこの順で積層され積層構造を形成している請求項4記載の二次電池。

【請求項15】 前記高分子膜が正の電荷を有するカチオン性高分子ゲルからなる請求項14記載の二次電池。

【請求項16】 セパレーターを有し、前記正極、前記高分子膜、セパレーター、前記負極がこの順で積層され積層構造を形成している請求項4記載の二次電池。

【請求項17】 前記高分子膜が負の電荷を有するアニ

オン性高分子ゲルからなる請求項16記載の二次電池。

【請求項18】 前記高分子膜が電池のセパレータの機能をも有し正極及び負極間に挟持されている請求項4記載の二次電池。

【請求項19】 前記高分子膜が孔径2~1000Åの細孔を有する請求項4記載の二次電池。

【請求項20】 前記高分子膜における高電界が局部的に印加及び／又は温度が局部的に上昇した際の細孔の径の収縮割合が元の細孔径の20~98%である請求項4記載の二次電池。

【請求項21】 前記二次電池の充電時における負極が、少なくともリチウム元素を含有する請求項1記載の二次電池。

【請求項22】 前記二次電池の充電時における負極が、少なくとも亜鉛元素を含有する請求項1記載の二次電池。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は二次電池に関し、より詳細には充放電の繰り返しによって発生するリチウム又は亜鉛のデンドライト（樹枝状）成長を抑えた二次電池に関する。

【0002】

【従来の技術】最近、大気中に含まれるCO<sub>2</sub>ガス量が増加しつつある為、温室効果により地球の温暖化が生じると予測されている。火力発電所は化石燃料などを燃焼させて得られる熱エネルギーを電気エネルギーに変換しているが、燃焼によりCO<sub>2</sub>ガスを多量に排出するため、新たな火力発電所は、建設することが難しくなっている。したがって、火力発電所などの発電機にて作られた電力の有効利用として、余剰電力である夜間電力を一般家庭に設置した二次電池に蓄えて、これを電力消費量が多い昼間に使用して負荷を平準化する、いわゆるロードレベリングが提案されている。

【0003】また、CO<sub>x</sub>、NO<sub>x</sub>、CH<sub>4</sub>などを含む大気汚染物質を排出しないという特徴を有する電気自動車の用途では、高エネルギー密度の二次電池の開発が期待されている。さらに、ブック型パーソナルコンピュータ、ワードプロセッサ、ビデオカメラ及び携帯電話などのポータブル機器の電源用途では、小型・軽量で高性能な二次電池の開発が急務になっている。

【0004】上記小型・軽量で高性能の二次電池としては、例えば、充電時の反応でリチウムイオンをデインターカレートするリチウムインターカレーション化合物を正極物質に、リチウムイオンを炭素原子で形成される六員環状平面の層間にインターカレートできる、グラファイトに代表されるカーボン材料を負極物質に用いたロッキングチェア型のいわゆる“リチウムイオン電池”の開発が進み、一部実用化されている。

【0005】しかし、上述した“リチウムイオン電池”

では、カーボン材料で構成された負極は、理論的には1原子あたり最大1/6のリチウム原子しかインターカレートできないため、例えば金属リチウムを負極物質に使用したときのリチウム一次電池に匹敵する高エネルギー密度の二次電池は実現できない。仮に充電時に負極のカーボンの層間に挿入できるリチウム量以上のリチウムを貯蔵しようとするカーボンの表面に金属リチウムがデンドライト成長して、短絡の原因となるので、層間に挿入できるリチウム量以上を貯蔵した高容量の二次電池は実現できていない。

【0006】一方、リチウム金属を負極に用いる高容量のリチウム電池では、充放電の繰り返しによって、短絡の主原因になるリチウムのデンドライトが発生し易く、このリチウムのデンドライト成長を抑えることが容易ではなく、リチウム電池の二次電池化を難しくしている。

【0007】また、充電時にリチウム金属が析出する、リチウム金属やアルミニウムなどの金属を負極に用いたリチウム二次電池も高エネルギー密度が期待できるので研究されているが実用領域までの寿命を有したものは実用化されていない。

【0008】負極にカーボンを用いた二次電池でも、負極に充電時にリチウム金属が析出する負極を用いた二次電池でも、リチウムのデンドライトが成長して、負極と正極が短絡状態になった場合には、電池の持つエネルギーが短時間で消費されることによって発熱し、電解液の溶媒が分解しガスを発生することによって内圧が高まり、仕舞には電池を破壊してしまう場合がある。この対策として、上記リチウムイオン電池をも含めたりチウム二次電池（以下ではリチウムイオンの酸化還元反応を利用した二次電池を総称して以下リチウム二次電池と呼ぶことにする）の安全性確保のために、正極、負極間のセパレーターに融点が120℃～170℃のポリエチレンやポリプロピレンの多孔性フィルムを使用し、電池が何らかの原因で短絡して内部温度が材料の融点まで上昇するとセパレーターが融けて孔がふさがり負極と正極を電気的に絶縁して電池反応が停止する仕組みが試みられている。しかし、万が一の安全対策にはなっていないが、リチウム二次電池における負極の寿命を飛躍的に伸ばす決定的な方法となり得ていない。

【0009】また、上述した有機ポリマーからなる多孔性フィルムをセパレーターとして用いたリチウム二次電池では電池の温度が120℃以上の高温にならないと機能しないこと、一旦溶融して孔のふさがったセパレーターでは温度が下がっても正極、負極間の絶縁状態が残り電池の性能は回復しない。このことから、電池の高容量化が実現でき、かつ充電時にリチウムのデンドライト成長を抑え、サイクル寿命も伸ばすことができる手段の開発が望まれている。

【0010】また、ニッケル亜鉛電池、空気亜鉛電池からなる二次電池においても、リチウム二次電池と同様に

充放電の繰り返しによって、亜鉛のデンドライトが発生し、セパレータを貫通して、亜鉛負極と正極が短絡してしまうため、サイクル寿命が短いという上述したリチウム二次電池と同様な問題があった。したがって、リチウム二次電池や亜鉛二次電池では、高容量化で十分なサイクル寿命が得られるものが強く望まれている。

【0011】

【発明が解決しようとする課題】本発明は、上記問題点に鑑みてなされたものであり、負極活物質がリチウム又は亜鉛である二次電池において、サイクル寿命が長く、且つ高エネルギー密度の二次電池を提供することを目的とする。

【0012】

【課題を解決するための手段】本発明の二次電池は、負極と、正極と、該正極及び負極間において、電解質と、電池反応に関与するイオンが移動可能であり環境に応じて変動可能な孔径の連通孔を有する層と、これらを収容する電池ハウジングとを有することを特徴とする二次電池である。尚、“電池反応に関与するイオン”とは、二次電池の充放電反応において、酸化・還元を受け、かかる反応に関与するイオンである。

【0013】本発明の二次電池は、正極及び負極間に介在する層において、電池反応に関与するイオンが移動可能であり環境に応じて変動可能な径（幅）を有し、正極及び負極間に通ずる連通孔（貫通孔）が存在する点で特徴的である。ここで“連通孔”とは二次電池における正極、負極間を連通する孔であり、電池反応に関与するイオンが当該連通孔をとって正極負極間を移動する通路となり得るものである。かかる連通孔は、特に上記正極、負極間のそれが存在する位置近傍に於ける電圧及び温度の変化に応じてその径（幅）が変動し、当該連通孔での正極及び負極間の抵抗を変化させる。例えば、電池反応において、一連通孔の周辺において電圧が局部的に高く、及び/又は温度が高い場合においては、当該連通孔の幅が狭くなるように変化し、当該連通孔付近における抵抗が高くなり、電池反応の進行が抑えられる。

【0014】二次電池の充電反応では、正極及び負極が表面形状や組成に関して不均一に形成されている等の影響により、正極及び負極間で局所的に高電界が生じ、局所的に温度が上昇し、反応が過度に進行し、電池の構成材料及び反応機構によっては、前述したような負極活物質デンドライト状に成長したり電解質の分解が生じたりすることがある。ひいてはこのような箇所では正極及び負極間の短絡に至る可能性が強くなる。従って、電池の正極、負極間の領域を、上記高電界又は温度上昇が生じる箇所の近傍での抵抗が上昇するように幅が変動する連通孔から構成するようにすることで、電池反応の進行の抑制に伴い、短絡が防止される。

【0015】本発明の二次電池は、高エネルギー密度が期待できる電池であって上述したデンドライト成長が抑

制されるものであり、好ましくは充電時の負極において少なくともリチウム元素を含むもの（リチウム二次電池）あるいは少なくとも亜鉛元素を含むもの（亜鉛二次電池）として用いる。

【0016】本発明の二次電池においては、前記正極及び負極間の層が、細孔を有し、電界強度が周囲より高い箇所、その細孔径が減少する高分子膜、または細孔を有し、周囲より温度上昇が大きい箇所、その細孔径が減少する高分子膜からなるものが好ましい。

【0017】上記の高分子膜が少なくとも高分子液晶または高分子と液晶の複合体から構成されているのが好ましい。そして、その高分子膜の液晶部が、電圧が印加されていない休止時には負極平面に垂直配向か若しくは傾斜配向しており、活物質のデンドライト成長の起こりやすい箇所、充電時に局部的に高電界が印加されるか及び／又は温度上昇が起こると、負極平面に平行配向か若しくは無秩序（ランダム）に配向し、細孔部の負極平面方向の長さ（細孔径）を減少させることが好ましい。高分子膜の高分子液晶または液晶が、少なくとも負の誘電異方性を有する液晶から構成されているのが好ましい。

【0018】また、上記の高分子膜が、少なくとも高分子ゲルから構成されているのが好ましい。

【0019】本発明者は、負極に金属リチウムやアルミニウムやカーボン材料を用いた、リチウム二次電池の充電時に、リチウムのデンドライトの成長が起こる箇所や条件を綿密に調査したところ、リチウムのデンドライト（樹枝状）成長し易い箇所は負極表面の突起部などの電界強度が高い箇所であり、大きな電流が流れて発熱していることを見いだした。負極に亜鉛を用いたニッケル亜鉛二次電池、空気亜鉛電池においても同様な所見が得られた。この知見に基づいて、選択的に上記箇所の抵抗を高めることを見出し、充電時にリチウムや亜鉛のデンドライト成長が抑制されることを確認したものである。

【0020】本発明の二次電池では、負極活物質がリチウムあるいは亜鉛の二次電池において、負極表面の突起部などの電界強度が高い箇所及び／又は局所的に温度上昇が激しい箇所、負極正極間の連通孔の孔径が狭くなるような連通孔からなる層を備え、当該連通孔で抵抗を高めて短絡を防止する。こうして、充電時にリチウムあるいは亜鉛がデンドライト状に成長するのを抑えることができ、その結果、充放電時のサイクル寿命を飛躍的に伸ばすことができる。したがって、これにより、サイクル寿命の長い高エネルギー密度の二次電池が実現できる。

【0021】尚、本発明において、“活物質”とは電池における充電及び放電の電気化学的可逆反応（の繰り返し）に関与する物質であり、更に自身で上記反応に関与する物質である限り、上記反応に関与する他の物質を保持する物質をも包含する。尚、リチウム二次電池では、負極活物質としてリチウムが充電時に負極側に保持さ

れ、放電時に電解液中に溶解してリチウムイオンとなる。また、亜鉛二次電池では、負極活物質として亜鉛が放電時に水酸イオンと反応して水酸化亜鉛又は酸化亜鉛に変化する。

【0022】

【発明の実施の形態】以下、本発明の実施態様例を、図1と図2及び図5を参照して説明する。図1は、本発明の二次電池の一例の断面を示す概念図である。同図1に示す本発明の二次電池は、負極101は、電解液を保持したあるいは電解質を兼用するセパレータ103を介して正極102と対向し、かつ対向する負極101と正極102の間に本発明の特徴である電池反応に関与するイオンが移動可能であり環境に応じて変動可能な孔径の連通孔を有する、特に電解強度や温度の高い領域で径

（幅）が小さくなり抵抗が高くなる連通孔を有する層として、細孔を有するポーラスな高分子膜100が設けられた構造体が電池ハウジング104内に収容されたものである。ポーラスな高分子膜100は電池反応に伴うイオンが通過できるが、高電界が印加されるところ及び温度が上昇したところでは細孔がせばまって、電池反応に伴うイオンの通過が制御され充電時に析出する金属の透過を制限するように成り、抵抗が高まる機能を有している。尚、正極102に接続した正極端子106、及び負極101に接続した負極端子105が各々ハウジング104外に引出されている。

【0023】この機能を図5を用いて説明する。図5は本発明の二次電池の機能を説明する概念図であり、図1の本発明の二次電池に直流電源を接続して充電する場合の一例である。図1の二次電池の負極表面に突起のような電界強度の高い箇所である電界集中部107が存在した場合、該電界集中部107では周辺より高電界が印加され、そのため電流密度が高くなり発熱する、その時、高分子膜100の高電界が印加され温度が上昇する箇所108では細孔が狭められ抵抗が上昇し、結果として負極表面の高電界が印加される箇所の電界集中部107では充電時にデンドライト状の負極活物質の析出が抑えられ、負極と正極間の内部短絡が抑えられることになるのである。

【0024】図2は、本発明の二次電池内の負極、正極、セパレータと、負極活物質のデンドライト成長を防止する手段である高分子膜の配置例を示す概念図である。図2の（a）、（b）および（c）は、各々図1の二次電池の断面における、負極101、正極102、セパレータ・電解液103、ポーラスな高分子膜100の配置例を示したものである。図2の（a）では、上記高分子膜100が負極101とセパレータ103間に設けられた例である。図2の（b）では、上記高分子膜100が正極102とセパレータ103間に設けられた例である。図2の（c）では、上記高分子膜100がセパレータ103を兼用して負極101と正極102間に設け

られた例である。

【0025】本発明の二次電池は、少なくとも正極及び負極、及び正極及び負極間において上述したような連通孔を有する層、具体的にはポーラスな高分子膜、電解質を有し、更にセパレーターや電池ハウジングを有するが、以下に各構成部分について説明する。

【0026】(高分子膜)本発明の特徴である二次電池を構成する負極と正極間に設ける、電池反応に関与するイオンが移動可能であり、環境に応じて変動可能な径

(幅)を有する連通孔からなる領域層であって、充電時の負極活性物質のデンドライト成長を防ぐため層としてのポーラスな高分子膜(図1で示す例では膜100)の機能としては、電池反応に関与するイオンを透過する細孔を有し、高電界が印加されるか、若しくは温度が上昇するとその細孔径が狭まる特性を有していることが必要である。

【0027】高分子膜の材質としては、例えば液晶高分子、母材と成る高分子と液晶との複合材、高分子ゲルが使用できる。上記高分子膜の材料の液晶高分子あるいは母材と成る高分子と液晶との複合材の液晶としては、電界が印加されると電界と垂直に分子の長軸が並び液晶が好ましく、誘電異方性が負の液晶がより好ましい。高分子膜の液晶部分の分子の長軸が電界と垂直方向に並ぶことによって、電界方向に貫通する細孔(上述した連通孔)が狭められることになる。また、上記高分子膜を形成する高分子ゲルでは温度上昇によって20%以上の大きな体積膨張が起こることが好ましくは必要である。体積膨張によって高分子ゲル内の細孔が狭められることになる。

【0028】さらに、この高分子ゲルを負極側に設ける場合は正の電荷を有するカチオン性高分子ゲルであることが望ましい。充電時に負極表面近傍にはリチウムカチオンが集まり、中和条件を保つためにカチオン性高分子ゲルは分子を伸ばして膨張する。この高分子ゲルを正極側に設ける場合は負の電荷を有するアニオン性高分子ゲルであることが望ましい。充電時には正極表面近傍にはアニオンが集まり、中和条件を保つためにアニオン性高分子ゲルは分子を伸ばして膨張する。

【0029】上述したように、本発明の二次電池を構成する特徴的な高分子膜の細孔が該細孔付近に局部的に高電界が生じた際に、又は温度上昇が生じた際に狭められることによって、電池反応に寄与するイオンや充電時に析出する負極活性物質が高分子膜とセパレータの細孔を貫通して正極まで到達して内部短絡するのを防ぐことができる。

【0030】なお、高分子膜に形成される細孔の径の大きさとしては電池反応に関与するイオンを透過する大きさであればよく、通常1 $\mu$ m以下、好ましくは2~100Åとする。

【0031】また、高分子膜の細孔は、高電界が印加さ

れるか、若しくは温度が上昇するとその細孔径が狭まるが、その細孔の径の収縮割合はイオンが移動する時の抵抗を上昇させるための機能が得られる範囲であればよく、通常は収縮分の元の細孔径に対する比率として10%以上、好ましくは20~98%が望ましい。

【0032】上述したような高分子膜を特にリチウム二次電池に採用する場合には、少なくとも電池に組み込み電解液を注入する前に、当該膜について減圧乾燥などの方法で十分水分を除去しておく必要がある。もし、脱水が十分に行われていなかったとしたら、充電時に析出するリチウムとこの水分が反応して、放電時に利用できない水酸化リチウムなどのリチウム化合物が形成され、放電電量の低下をもたらすことになる。

【0033】高分子液晶材料を使用して上記連通孔を有するポーラスな高分子膜を形成する方法としては、高分子液晶材料を溶剤に溶解した溶液を、キャスト法によって膜形成をするか、あるいは直接負極、セパレータ、正極表面に塗布して膜を形成する。ついで乾燥して溶媒を除去し、細孔を形成する。高分子液晶材料を用いて形成する他に、高分子液晶が重合反応で得られるモノマーを使用して重合反応と同時に高分子膜を形成することも可能である。また、場合によっては細孔分布を調整するために、膜形成時に抽出除去できる例えば電解質などを添加して膜形成し、乾燥後にさらに膜調製時に添加した物質を抽出除去して細孔分布を調整する。

【0034】細孔の調製方法としては、後ほど除去可能な物質を高分子膜形成時に所望な多孔率に成るように添加した後、必要に応じて溶媒を添加して、膜形成時あるいは後に除去可能な物質を除去して細孔を調製する。除去可能な物質としては、溶出可能な例えば電解液に使用する電解質や有機溶媒が挙げられる。電解質を除去可能な添加物質に用いた場合には電池特性に与える影響が少ない。別の除去可能な物質として加熱か減圧下で蒸発または分解させて除去するか、除去する溶媒と均一に混合する沸点の低い溶媒を用いることも可能である。

【0035】膜形成後に電解液に対する溶解安定性を増すために、架橋反応を起こして架橋させることも好ましい。架橋方法としては、膜形成時に架橋剤を添加し架橋反応を起こす、若しくは膜形成後に紫外線や放射線を照射して架橋反応を起こす方法が挙げられる。

【0036】高分子材料と液晶材料の複合体で上記連通孔を有するポーラスな高分子膜を形成する方法としては、母材となる高分子を溶媒に溶解した高分子溶液に、液晶材料を混合し、得られた混合溶液を回転する平坦で均一な金属支持体上に流延してフィルム化するキャスト法によって、あるいは直接負極、セパレータ、あるいは正極表面に塗布して膜を形成して乾燥して溶媒を除去して高分子膜を調製する。場合によっては上述の高分子液晶膜形成のように、細孔分布の調整のために、後ほど除去可能な例えば電解質のような添加物質を添加し

て、高分子膜形成を行うことも可能である。さらに、膜形成後に架橋反応を起こして架橋させることも、電解液に対する安定性を増すために、好ましい。架橋方法としては、前述の高分子液晶膜の架橋方法と同様な方法が採用できる。

【0037】本発明の二次電池において、正極、負極間の環境に応じて孔（幅）の変動可能な連通孔を有する層領域として用いる高分子膜である、上記高分子液晶膜、高分子と液晶の複合膜の液晶は、膜形成時に負極電極平面に垂直配向若しくは傾斜配向をさせておくことが好ましい。

【0038】配向方法としては、上記高分子膜固化前に磁場若しくは電界を負極電極平面に垂直方向若しくは傾斜あるいは平行方向に印加する方法を用いることができる。その他の配向方法としては、応力印加、膜を形成する基体表面の配向処理、加熱もしくは冷却、最適溶媒及び最適濃度の選択等によって制御される。

【0039】上記膜を形成する基体表面の配向処理の具体例としては、垂直配向の処理方法としては、 $p$ -（オクチルオキシ）- $p'$ -ヒドロキシアゾベゼン、ジメチルヘキサデシルアンモニウムブロマイド、 $N$ -[11-プロモウンデカノイル]- $\alpha$ -ヒドロキシ酸ジドデシルエステル、ヘキサデシルトリブチルホスホニウムブロマイド、ステアリルトリブチルホスホニウムブロマイド、レシチン、セチルトリメチルアンモニウムブロマイドなどの両親媒性分子の物理吸着やステリルトリクロシランなどの有機金属カップリング剤の化学吸着が挙げられる。

【0040】傾斜配向としては、基体表面に、金属若しくは有機高分子をスパッタリングや電子ビーム蒸着等の真空蒸着方法で斜め蒸着して配向膜を形成する方法が挙げられる。

【0041】一方、高分子ゲル材で上記連通孔を有するポーラスな高分子膜を形成する方法としては、（a）モノマーから直接重合と架橋反応で高分子ゲルを形成するか、高分子を形成した後に架橋反応を起こし高分子ゲルを形成する、（b）モノマー溶液中にセパレータを浸漬した後架橋反応で高分子ゲルを形成するか、高分子溶液中にセパレータを浸漬した後に架橋反応を起こし高分子ゲルを形成する、（c）モノマーから重合と架橋反応で高分子ゲル粉を形成した後、高分子溶液中に高分子ゲル粉を分散させ固化して形成する、（d）負極表面、正極表面、あるいはセパレータ表面上に高分子溶液をキャストした後に架橋反応にて高分子ゲルを形成するか、モノマー溶液をキャストした後に重合反応と架橋反応を起こし高分子ゲルを形成する。高分子ゲルの厚みは重合時あるいは架橋時の形成時に調節してそのまま使用するか、形成後に乾燥プレス加工などで厚みを均一に調整して使用する。高分子ゲルの厚みは、形成時の溶媒種と濃度、反応容器の深さなどで調整することができ

る。高分子ゲルの膨張率は、モノマー種、重合度、架橋度、溶媒の種類と濃度、溶媒に含まれる電解質濃度などで、調整することができる。

【0042】その他の上述した高分子液晶、高分子と液晶の複合体、又は高分子ゲルにより形成されるポーラスな高分子膜を、フィルム若しくはシートとして作製する方法としては、溶媒で溶解した高分子溶液を回転する平坦で均一な金属支持体上に流延してフィルム化するキャスト法（溶液流延法）の他に、熱で溶解した高分子溶液をT型ダイスから押し出してフィルム化するエクストルージョン法（溶融押出法）、2本以上のロールの間で高分子物質を圧延してフィルム化するカレンダー法が使用できる。エクストルージョン法では架橋前の高分子を使用し、フィルム化した後に架橋反応を起こして、高分子フィルムを得る。カレンダー法では乾燥した高分子を用いてフィルムを作製する。

【0043】（液晶材料）前述したポーラスな高分子膜の材料となる高分子有機液晶、又は高分子と液晶の複合体に用いる液晶材料としては、例えば融解過程を経て液晶層を呈するサーモトロピック材料、溶媒の存在下で液晶性を示すライオトロピック材料をも包含される。用いられる液晶の配向の種類としては、ネマチック液晶、コレステリック液晶、スメチック液晶、ディスコチック液晶、自発分極を示す強誘電液晶、などが挙げられるが、負の誘電異方性を示す液晶であることが好ましく、ネマチック液晶相若しくはコレステリック液晶相を示すのがより好ましい。

【0044】また、電圧が印加されていない休止時には負極平面に液晶部が垂直配向か若しくは傾斜配向しており、充電時に局部的に高電界が印加され温度上昇が起こる活物質のデンドライト成長の起こりやすい箇所を負極平面に平行配向か若しくは無秩序に配向するのがより好ましい。

【0045】さらに、二次電池の使用温度に合わせて機能するように、複数の液晶をブレンドして使用するのが好ましい。上記液晶は二次電池の負極平面に垂直な配向処理若しくは傾斜配向処理が施され、初期状態での上記液晶の配向（負極面に対して垂直ないしは傾斜配向）が施されることが好ましい。これらの配向処理による初期状態での液晶分子の負極平面に対するチルト角は $45^\circ$ 以上である。

【0046】本発明に使用する上記負の誘電異方性を示す液晶材料としては、2, 3-ジフロロベンゼン誘導体、ピリダジン誘導体、フッ素化ヒドロキノンシクロヘキサカルボン酸エステル化合物、フッ素化トラン化合物、シアノベンゼンカルボン酸エステル化合物、シアノシクロヘキサ化合物、などが挙げられ、その中でも、3, 6-2置換-1, 2-ジシアノベンゼン類、3, 6-2置換ピリダジン、3, 6-2置換-1, 2-ジフロロベンゼン類、3, 6-2置換-1-シアノベンゼン

類、1, 4-2置換-1-シアノシクロヘキサン類、などが比較的大きな負の誘電異方性を示す例として挙げられる。

【0047】本発明に用いる上記液晶高分子の構造は、直線性共役形の原子団であるメソゲン基が、あるいはメソゲン基とアルキル鎖かオキシエチレン鎖が交互に直線的に結合した主鎖形重合体と、メソゲン基が直接あるいはアルキル鎖を介して主鎖に側鎖として結合した側鎖形重合体がある。上記メソゲン基としては、ベンジリデンアニリン、アゾベンゼン、アゾキシベンゼン、スチルベン、フェニルベンゾエート、ベンゾイルアニリン、ビフェニル、ベンジリデンアセトフェノン、ベンジリデンアジン、などが挙げられる。

【0048】(高分子-液晶複合体における高分子) 前述したポーラスな高分子膜となる高分子と液晶の複合体における固体となる高分子材料としては、電池の電解液に不溶である高分子材料、また架橋させて電解液に不溶とした高分子材料を用いることができる。更に、高分子-液晶複合体の調製に用いる溶媒に可溶な有機高分子あるいはその原料モノマーを用いることができる(モノマーを用いた場合は複合体の調製段階で重合する)。上記高分子材料の例としては、ポリエチレンやポリプロピレン等のポリオレフィン、フッ素樹脂、ポリ塩化ビニル、ポリビニルアルコール、ポリアクリルアミド、ポリエステル、ポリアミド、ポリエチレンオキサ이드等が挙げられる。

【0049】(高分子ゲル) 本発明において、前述したポーラスな高分子膜の材料となる高分子ゲルとしては、好ましくはリチウム二次電池の内部短絡防止手段を構成する、溶媒に不溶の三次元網目構造を有している高分子または溶媒を吸って膨潤状態にあるものが用いられる。

【0050】かかる高分子ゲルとしては、例えばポリアクリルアミド、N, N-ジエチルアクリルアミドポリマー、N-イソプロピルアクリルアミドポリマー、N-イソプロピルアクリルアミド-アクリル酸ナトリウム共重合体、N, N-ジエチルアクリルアミド-アクリル酸ナトリウム共重合体、アクリルアミド(メタクリルアミドプロピル)トリメチルアンモニウムクロライド共重合体、アクリルアミド-トリメチル(N-アクリロイル-3-アミノプロピル)アンモニウムヨウダイド共重合体、ポリスチレン、スチレン-スチレンサルフォネート共重合体、ポリビニルメチルエーテル、ポリビニルアルコール-ポリアクリル酸複合ゲル、ポリアクリル酸、ポリメタクリル酸、メタクリル酸-2-ヒドロキシエチル、セルロース、ポリエチレングリコール、ポリエチレンオキサイド、ポリビニルアルコール、などが挙げられる。これらの内、N-イソプロピルアクリルアミド-アクリル酸ナトリウム共重合体、N, N-ジエチルアクリルアミド-アクリル酸ナトリウム共重合体、アクリルアミド(メタクリルアミドプロピル)トリメチルアンモ

ニウムクロライド共重合体、アクリルアミド-トリメチル(N-アクリロイル-3-アミノプロピル)アンモニウムヨウダイド共重合体、スチレン-スチレンサルフォネート共重合体、などのイオン解離基を有した高分子ゲルが、好ましく用いられる。また上記高分子ゲルの内、常温で高分子鎖が収縮した状態であるポリアクリルアミド、N, N-ジエチルアクリルアミドポリマーのような高分子ゲルも高温で膨張するので本発明に使用するのに好ましい。

【0051】本発明で使用可能な高分子ゲルの形成方法としては、例えば化学結合により又は分子間結合によるものが採用される。化学結合によってゲルを形成する方法としては、重合反応時に架橋する方法、重合後に架橋する方法があり、分子間の結合によって高分子鎖間を架橋する方法としては、水素結合による架橋、イオン結合による架橋、配位結合による架橋がある。

【0052】また、架橋による方法には、例えばジビニル化合物や多官能性化合物の重合による橋かけ構造の形成、熱、光、放射線、プラズマなどのエネルギーにより重合と橋かけを同時に行うまたは直鎖状高分子を合成した後橋かけする方法もある。

【0053】重合反応時に橋かけする方法としては、例えばエチレングリコールジメタクリレートやメチレンビスアクリルアミドを橋かけ剤としてラジカル開始剤による重合、ガンマ線や電子線を照射する放射線重合、ビニルモノマーの吸収波長と一致する光を橋かけ剤存在下で照射するか光増感剤を加え光照射する光重合が挙げられる。

【0054】高分子鎖間を後で橋かけする方法としては、例えば水酸基を有するセルロースやポリビニルアルコールをアルデヒド、N-メチロール化合物、ジカルボン酸、ビスエポキシドなどの化学反応で架橋する、アミノ酸を有する高分子はアルデヒドやグリシジル基によってゲル化する方法、ガンマ線などの放射線照射でポリビニルアルコールやポリメチルビニルエーテルを水中で架橋する方法、ポリビニルアルコールやN-ビニルピロリドンを経アゾ樹脂、ビスアジド、重クロム酸塩などの光橋かけ剤で橋かけする、ポリビニルアルコールなどの水溶性高分子にスチルバゾリウム塩などの感光基を持つポリマーを光二量化する、気体の放電によって生成したプラズマを高分子材に接触させて橋かけする方法が挙げられる。

【0055】高分子間の水素結合やイオン結合、キレート形成などによってもゲルを形成することができ、凍結真空乾燥法、凍結解凍法などによって高分子間に水素結合を形成させる、また、ポリメタクリル酸とポリエチレングリコール、ポリアクリル酸とポリビニルアルコールのように二種類の異なった高分子を混合することによってゲルを形成することができる。ポリビニルベンジルトリメチルアンモニウムなどのポリカチオンとポリスチレ



ンスルホン酸ナトリウムなどのポリアニオンを混合することによってポリイオンコンプレックスゲルを形成することができる。ポリアクリル酸などのポリカルボン酸やポリスチレンスルホン酸などの強酸性ポリマーはアルカリ、アルカリ土類金属と結合させてゲルを形成することができる。

【0056】（負極）本発明の二次電池における負極材料（図1に示す例では負極101）の材料として、好ましくは充電時にリチウム元素を含むものが用いられ（リチウム二次電池）、あるいは亜鉛元素を含むものが用いられる（亜鉛二次電池）。好ましくは負極材料を集電体上に成形することで負極が得られている。

【0057】リチウム二次電池用の負極材料としては、例えば、リチウム金属、黒鉛を含めた炭素材料、金属材料、遷移金属化合物のようなリチウムがインターカレートする材料が挙げられる。上記金属材料としては、リチウムと合金を形成するアルミニウムなどの金属材料、析出するリチウムを収納する細孔を有し集電体をも兼ねる多孔質のニッケルなどの金属などが好適である。

【0058】上記負極用材料の形状としては箔や板状であればそのまま用いることができる。また、粉末状であれば結着剤を混合し、場合によっては導電補助材も添加して、集電体上に塗膜を形成して負極を作成する。また、集電体上に上記材料の薄膜を形成する方法としてはメッキや蒸着法を用いることもできる。上記蒸着方法としては、CVD（Chemical Vapor Deposition）、電子ビーム蒸着、スパッタリングなどの方法が挙げられる。いずれのリチウム二次電池用の負極も減圧下で十分に乾燥することが必要である。

【0059】亜鉛二次電池用の負極としては、亜鉛の箔や板、集電体上に亜鉛のメッキ膜あるいは蒸着膜を形成したもの、酸化亜鉛粉あるいは亜鉛粉と酸化亜鉛粉に結着剤を混合し（場合によっては導電補助材を添加して）集電体上に塗膜を形成したものを、負極に使用できる。

【0060】（正極）本発明の二次電池における正極（図1に示す例では正極102）は、集電体、正極活物質、導電補助材、結着剤などの材料から構成されたものである。この正極は、正極活物質、導電補助材及び結着剤などを混合したものを、集電体の表面上に成形して作製される。

【0061】正極に使用する導電補助材としては、黒鉛、ケッチェンブラックやアセチレンブラックなどのカーボンブラック、ニッケルなどの金属微粉末などが挙げられる。

【0062】正極に使用する結着剤としては、例えば、電解液が非水溶液系の場合には、ポリエチレンやポリプロピレンなどのポリオレフィン、又はポリフッ化ビニリデンやテトラフルオロエチレンポリマーのようなフッ素樹脂、電解液が水溶液系の場合には、ポリビニルアルコール、セルロース又はポリアミドなどが挙げられる。

【0063】負極活物質がリチウムであるリチウム二次電池では、正極活物質としては、遷移金属酸化物、遷移金属硫化物、リチウム-遷移金属酸化物、又はリチウム-遷移金属硫化物が一般に用いられる。遷移金属酸化物や遷移金属硫化物の遷移金属元素としては、例えば、部分的にd殻あるいはf殻を有する元素であるところの、Sc, Y, ランタノイド, アクチノイド, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Auが挙げられる。特に、第一遷移系金属であるTi, V, Cr, Mn, Fe, Co, Ni, Cuが好適に用いられる。

【0064】負極活物質が亜鉛であるニッケル亜鉛二次電池では、正極活物質としては、酸化水酸化ニッケルを用いる。

【0065】負極活物質が亜鉛である空気亜鉛二次電池では、正極活物質としては酸素を用い、正極は集電体と触媒と撥水材から構成されている。触媒としては、例えば、多孔質炭素、多孔質ニッケル、酸化銅、酸化ニッケルが用いられる。撥水材としては、多孔質のテトラフルオロエチレンポリマーやポリフッ化ビニリデンのようなフッ素樹脂が用いられる。負極活物質が亜鉛である亜鉛酸素二次電池では、正極活物質としては酸素を用いる。

【0066】（負極及び正極の集電体）本発明の二次電池における負極及び正極で用いる集電体は、充放電時の電極反応で消費する電流を効率よく供給するあるいは発生する電流を集電する役目を担っている。したがって、負極及び正極の集電体を形成する材料としては、電導度が高く、かつ、電池反応に不活性な材質が望ましい。

【0067】好ましい材質としては、ニッケル、チタニウム、銅、アルミニウム、ステンレススチール、白金、パラジウム、金、亜鉛、各種合金、及び上記材料の二種以上の複合金属が挙げられる。集電体の形状としては、例えば、板状、箔状、メッシュ状、スポンジ状、繊維状、パンチングメタル、エキスパンドメタルなどの形成状が採用できる。

【0068】（セパレータ）本発明の二次電池におけるセパレータ（図1に示す例では103）は、負極と正極間に配置され、これらの短絡を防ぐ役割がある。また、電解液を保持する役割を有する場合もある。

【0069】セパレータは、リチウムイオンまたは水酸イオンが、移動できる細孔を有し、かつ電解液に不溶で安定である必要がある。したがって、セパレータとしては、例えば、ガラス、ポリプロピレンやポリエステルなどのポリオレフィン、フッ素樹脂、ポリアミドなどの不織布あるいはマイクロポア構造の材料が好適に用いられる。

【0070】また、微細孔を有する金属酸化物フィルム、又は金属酸化物を複合化した樹脂フィルムも使用できる。特に、多層化した構造を有する金属酸化物フィル



ムを使用した場合には、デンドライトが貫通しにくいいため、短絡防止に効果がある。難燃材であるフッ素樹脂フィルム、又は不燃材であるガラス、若しくは金属酸化物フィルムを用いた場合には、より安全性を高めることができる。

【0071】（電解質）本発明の二次電池における電解質は、例えば上述した電池反応に関与するイオンが移動可能であり、電圧又は温度といった環境に応じて変動可能な径を有する連通孔を有する層（図1に示す例では高分子膜100）及びセパレータ103に保持される。かかる電解質の使用法としては、次の3通りが挙げられる。

- （1）そのままの状態で用いる方法。
- （2）溶媒に溶解した溶液として用いる方法。
- （3）溶液にポリマーなどのゲル化剤を添加することによって、固定化したものとして用いる方法。

【0072】一般的には、溶媒に電解質を溶かした電解液を多孔性のセパレータに保液させて使用する。電解質の導電率は、25℃における値として、好ましくは $1 \times 10^{-3} \text{ S/cm}$ 以上、より好ましくは $5 \times 10^{-3} \text{ S/cm}$ 以上であることが必要である。

【0073】負極活物質がリチウムであるリチウム電池では、以下に示す電解質とその溶媒が好適に用いられる。電解質としては、例えば、 $\text{H}_2\text{SO}_4$ 、 $\text{HCl}$ 、 $\text{HNO}_3$ などの酸、リチウムイオン（ $\text{Li}^+$ ）とルイス酸イオン（ $\text{BF}_4^-$ 、 $\text{PF}_6^-$ 、 $\text{AsF}_6^-$ 、 $\text{ClO}_4^-$ 、 $\text{CF}_3\text{SO}_3^-$ 、 $\text{BPh}_4^-$ （ $\text{Ph}$ ：フェニル基））から成る塩、およびこれらの混合塩が挙げられる。また、ナトリウムイオン、カリウムイオン、テトラアルキルアンモニウムイオンなどの陽イオンとルイス酸イオンからなる塩も使用できる。上記塩は、減圧下で加熱したりして、十分な脱水と脱酸素を行っておくことが望ましい。

【0074】電解質の溶媒としては、例えば、アセトニトリル、ベンゾニトリル、プロピレンカーボネート、エチレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、ジメチルホルムアミド、テトラヒドロフラン、ニトロベンゼン、ジクロロエタン、ジエトキシンエタン、1,2-ジメトキシエタン、クロロベンゼン、γ-ブチロラクトン、ジオキソラン、スルホラン、ニトロメタン、ジメチルサルファイド、ジメチルサルオキシド、ギ酸メチル、3-メチル-2-オキダゾリジノン、2-メチルテトラヒドロフラン、3-プロピルシドノン、二酸化イオウ、塩化ホスホリル、塩化チオニル、塩化スルフリル又はこれらの混合液が使用できる。

【0075】上記溶媒は、例えば、活性アルミナ、モレキュラーシーブ、五酸化リン、塩化カルシウムなどで脱水するか、溶媒によっては、不活性ガス中でアルカリ金属共存下で蒸留して不純物除去と脱水をも行うのがよい。

【0076】電解液の漏洩を防止するために、ゲル化する

ことが好ましい。ゲル化剤としては電解液の溶媒を吸収して膨潤するようなポリマーを用いるのが望ましい。このようなポリマーとしては、ポリエチレンオキシド、ポリビニルアルコール、ポリアクリルアミドなどが用いられる。

【0077】負極活物質が亜鉛であるニッケル亜鉛電池や空気亜鉛電池では、以下に示す電解質が好適に用いられる。電解質の溶媒には水が用いられる。電解質としては、例えば、アルカリ（水酸化カリウム、水酸化ナトリウム、水酸化リチウムなど）が使用される。負極活物質が亜鉛である臭素亜鉛電池では、臭化亜鉛などの塩が使用される。

【0078】電解液の漏洩を防止するために、ゲル化することが好ましい。ゲル化剤としては電解液の溶媒を吸収して膨潤するようなポリマーを用いるのが望ましい。このようなポリマーとしては、例えば、ポリエチレンオキシド、ポリビニルアルコール、ポリアクリルアミドなどのポリマーや、デンプンが用いられる。

【0079】（電池の形状と構造）本発明の二次電池の具体的な形状としては、例えば、扁平形、円筒形、直方体形、シート形などがある。又、電池の構造としては、例えば、単層式、多層式、スパイラル式などがある。その中でも、スパイラル式円筒形の電池は、負極と正極の間にセパレータを挟んで巻くことによって、電極面積を大きくすることができ、充放電時に大電流を流すことができるという特徴を有する。また、直方体形やシート形の電池は、複数の電池を収納して構成する機器の収納スペースを有効に利用することができる特徴を有する。

【0080】以下では、図3と図4を参照して、電池の形状と構造についてより詳細な説明を行う。図3は単層式扁平形（コイン形）電池の断面図であり、図4はスパイラル式円筒形電池の断面図を表している。これらは基本的には図1と同様な構成で、負極、正極、電解質・セパレータ、電池ハウジング、出力端子を有する。

【0081】図3と図4において、301と402は負極（負極402は負極集電体400と活物質層401からなる）、303と408は正極（正極408は正極集電体404と活物質層403からなる）、305と405は負極端子（負極キャップ）、306と406は正極端子（正極缶）、307と407はセパレータ・電解液、310と410はガスケット、411は絶縁板、412は負極リード、413は正極リード、414は安全弁である。

【0082】図3に示す扁平型（コイン型）の二次電池では、正極活物質層を含む正極303と負極材料層を備えた負極301が少なくとも電解液を保持したセパレータ307、更には前述したような連通孔を有する層としての高分子膜315を介して積層されており、この積層体が正極端子としての正極缶306内に正極側から收容され、負極側が負極端子としての負極キャップ305に

より被覆されている。そして正極缶内の他の部分にはガスケット310が配置されている。

【0083】図4に示すスパイラル式円筒型の二次電池では、正極集電体404上に形成された正極（活物質）層403を有する正極と、負極集電体400上に形成された負極（活物質）層401を有した負極402が、少なくとも電解液を保持したセパレータ407、更には前述したような連通孔を有する層としての高分子膜415を介して対向し、多重に巻回された円筒状構造の積層体を形成している。当該円筒状構造の積層体が、正極端子としての正極缶406内に収容されている。また、当該正極缶406の開口部側には負極端子としての負極キャップ405が設けられており、負極缶内の他の部分においてガスケット410が配置されている。円筒状構造の電極の積層体は絶縁板411を介して正極缶及び負極キャップの内部と隔てられている。正極408については正極リード413を介して正極缶406に接続されている。又負極402については負極リード412を介して負極キャップ405と接続されている。負極キャップ側には電池内部の内圧を調整するための安全弁414が設けられている。

【0084】以下では、図3や図4に示した電池の組み立て方法の一例を説明する。

(1) 高分子膜（315、415）で被覆された負極層（301、401）と成形した正極層（303、403）の間に、セパレータ（307、407）を挟んで、正極缶（306、406）に組み込む。

(2) 電解質を注入した後、負極キャップ（305、405）とガスケット（310、410）を組み立てる。

(3) 上記（2）を、かしめることによって、電池は完成する。

【0085】なお、上述したリチウム電池の材料調製、および電池の組立は、水分が十分除去された乾燥空気中、又は乾燥不活性ガス中で行うのが望ましい。

【0086】上述した二次電池の例における部材の態様について説明する。

（ガスケット）ガスケット（310、410）の材料としては、例えば、ポリオレフィン樹脂、フッ素樹脂、ポリアミド樹脂、ポリスルホン樹脂、各種ゴムが使用できる。電池の封口方法としては、図3と図4のようにガスケットを用いた「かしめ」以外にも、ガラス封管、接着剤、溶接、半田付けなどの方法が用いられる。また、図4の絶縁板（411）の材料としては、各種有機樹脂材料やセラミックスが用いられる。

【0087】（電池ハウジング／正極缶、負極キャップ）本発明の二次電池で各部材を収容する電池ハウジングとしては、例えば、図3及び図4に示す例のように電池の各電極端子と正極缶及び負極キャップ等を兼用する。図3に示す例では正極缶306及び負極キャップ305が、図4に示す例では、正極缶406及び負極キャ

ップ405が、夫々出入口端子を兼ねる電池ハウジングとなる。出入口端子を兼ねる電池ハウジングの材料としては、ステンレススチールが好適に用いられる。特に、チタンクラッドステンレス板や銅クラッドステンレス板、ニッケルメッキ鋼板などが多用される。

【0088】特に図3と図4に示す例では正極缶306、406が電池ハウジングを兼ねているため、上記のステンレススチールが好ましい。一方、正極缶等が電池ハウジングを兼用しない場合には、電池ハウジングの材質としては、ステンレススチール以外にも例えば亜鉛などの金属、ポリプロピレンなどのプラスチック、又は金属若しくはガラス繊維とプラスチックの複合材が用いられる。

【0089】（安全弁）本発明の二次電池には、電池の内圧が高まった時の安全対策として、安全弁（図4に示す例では414）が設けられることが好ましい。安全弁としては、例えば、ゴム、スプリング、金属ボール、破裂箔などが使用できる。

【0090】

【実施例】以下、実施例に基づき本発明を詳細に説明する。なお、本発明はこれらの実施例に限定されるものではない。

【0091】実施例1

本発明では、図3に示した断面構造のようなコイン形のリチウム二次電池を作製した。負極表面には充電時のリチウムのデンドライト成長による内部短絡防止用の高分子一液晶複合膜で被覆した負極を用いた。以下では、図3を参照して、電池の各構成物の作製手順と、電池の組み立てについて説明する。なお、操作は全てアルゴンガス中で行った。

【0092】（1）負極（活物質）層301の作製手順  
①銅のエキスバンドメタルに金属リチウム箔を圧着して負極層301を作製した。

【0093】（2）高分子一液晶複合膜での負極の被覆  
ポリ塩化ビニルと負の誘電異方性を示すMerck社製液晶ZLI-4519を重量比40/60になるように混合した後、ジクロロエタンを添加して塗布溶液を調製した。

【0094】前記（1）で作製した銅のエキスバンドメタルに圧着した金属リチウム箔表面に、上記で調製した塗布溶液を塗布後、金属リチウム箔面に垂直方向に磁場を印加して乾燥し、次いで紫外線を照射して架橋させて液晶が分散した高分子膜315で被覆した金属リチウム箔の負極（活物質）層301を得た。

【0095】（3）正極（活物質）層303の作製手順  
電解二酸化マンガンと炭酸リチウムを、1:0.4のモル比で混合した後、800℃で熱処理して、リチウム-マンガン酸化物を調製した。

上記において調製したリチウム-マンガン酸化物に、アセチレンブラックの炭素粉3wt（重量）%とポ

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-298066

(43)Date of publication of application : 18.11.1997

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(51)Int. Cl. H01M 10/04

H01M 10/28

H01M 10/40

H01M 12/08

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(21)Application number : 09-065604 (71)Applicant : CANON INC

(22)Date of filing : 05.03.1997 (72)Inventor : KAWAKAMI SOICHIRO

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(30)Priority

Priority	08 73079	Priority	05.03.1996	Priority	JP
number :		date :		country :	

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(54) SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a secondary battery with long life and high density by interposing, between a positive electrode and a negative electrode, a layer having a communicating hole having a diameter variable according to the environment in which an ion participant in battery reaction is movable.

SOLUTION: A structural body formed of a positive electrode 102, a negative electrode 101 opposed to the positive electrode 102 through a separator holding an electrolyte or used also as the electrode, and a polymer film 100 provided between the opposed negative electrode 101 and positive electrode 102 is housed in a battery housing 104. The porous polymer film 100 has a function of transmitting ions accompanying a battery reaction, but narrowing the pores in parts where a high electric field is applied and the temperature is raised to limit the passing of the ions accompanying the battery reaction, thereby increasing the

resistance. Such polymer layer 100 is provided between the positive electrode 102 and the negative electrode 101, whereby a secondary battery with long life and high density can be provided.

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#### LEGAL STATUS

[Date of request for examination] 26.11.1998

[Date of sending the examiner's  
decision of rejection]

[Kind of final disposal of  
application other than the  
examiner's decision of rejection or  
application converted registration]

[Date of final disposal for  
application]

[Patent number] 3246596

[Date of registration] 02.11.2001

[Number of appeal against  
examiner's decision of rejection]

[Date of requesting appeal against  
examiner's decision of rejection]

[Date of extinction of right]

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#### CLAIMS

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[Claim(s)]

[Claim 1] The rechargeable battery characterized by having the layer which is movable between a negative electrode, a positive electrode, and this positive electrode and a negative electrode as for an electrolyte and the ion which participates in a cell reaction, and has the free passage hole of the aperture which can be changed according to an environment, and cell housing which holds these.

[Claim 2] Said free passage hole is a rechargeable battery according to claim 1 with which an aperture is changed according to change of the field strength in the field of this perimeter of a free passage hole, and/or temperature.

[Claim 3] Said free passage hole is a rechargeable battery according to claim 2 to which an aperture becomes small by the rise of the field

strength in the field of this perimeter of a free passage hole, and/or the rise of temperature.

[Claim 4] The rechargeable battery according to claim 1 whose layer which has said free passage hole is the poly membrane which has the pore to which a path is changed according to change of field strength and/or temperature.

[Claim 5] The rechargeable battery according to claim 4 to which a path becomes small by the rise of field strength [ in / in the pore in said poly membrane / the field of this perimeter of pore ], and/or the rise of temperature.

[Claim 6] The rechargeable battery according to claim 4 with which said poly membrane consists of a polymer liquid crystal.

[Claim 7] The rechargeable battery according to claim 6 in which said polymer liquid crystal carries out orientation in parallel or at random substantially to a negative-electrode flat surface in perpendicular orientation or the circumference of the pore which is carrying out inclination orientation, and which the rise of field strength and/or the rise of temperature produced to a negative-electrode flat surface in the bottom of no electric-field impressing.

[Claim 8] The rechargeable battery according to claim 6 whose dielectric constant anisotropy of said polymer liquid crystal is negative.

[Claim 9] The rechargeable battery according to claim 4 with which said poly membrane consists of complex of a macromolecule and liquid crystal.

[Claim 10] The rechargeable battery according to claim 9 in which the liquid crystal in said poly membrane carries out orientation in parallel or at random substantially to a negative-electrode flat surface in perpendicular orientation or the circumference of the pore which is carrying out inclination orientation, and which the rise of field strength and/or the rise of temperature produced to a negative-electrode flat surface in the bottom of no electric-field impressing.

[Claim 11] The rechargeable battery according to claim 9 whose dielectric constant anisotropy of the liquid crystal in said poly membrane is negative.

[Claim 12] The rechargeable battery according to claim 4 with which said poly membrane consists of polymer gel.

[Claim 13] The rechargeable battery according to claim 12 in which said polymer gel carries out cubical expansion 20% or more by the rise of temperature.

[Claim 14] The rechargeable battery according to claim 4 which it has a separator, and the laminating of said positive electrode, a separator, said poly membrane, and said negative electrode is carried out in this

order, and forms the laminated structure.

[Claim 15] The rechargeable battery according to claim 14 which consists of cationic polymer gel in which said poly membrane has positive charge.

[Claim 16] The rechargeable battery according to claim 4 which it has a separator, and the laminating of said positive electrode, said poly membrane, a separator, and said negative electrode is carried out in this order, and forms the laminated structure.

[Claim 17] The rechargeable battery according to claim 16 which consists of anionic polymer gel in which said poly membrane has negative charge.

[Claim 18] The rechargeable battery according to claim 4 with which said poly membrane also has the function of the separator of a cell, and is pinched between the positive electrode and the negative electrode.

[Claim 19] The rechargeable battery according to claim 4 which has the pore said whose poly membrane is 2-1000Å of apertures.

[Claim 20] The rechargeable battery according to claim 4 whose contraction rate of the path of the pore at the time of the high electric field in said poly membrane going up locally [ impression and/or temperature ] locally is 20 - 98% of the original pore diameter.

[Claim 21] The rechargeable battery according to claim 1 with which the negative electrode at the time of charge of said rechargeable battery contains a lithium element at least.

[Claim 22] The rechargeable battery according to claim 1 with which the negative electrode at the time of charge of said rechargeable battery contains a zinc element at least.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the rechargeable battery which suppressed dendrite (arborescence) growth of the lithium generated by the repeat of charge and discharge in a detail, or zinc more about a rechargeable battery.

[0002]

[Description of the Prior Art] CO<sub>2</sub> contained in atmospheric air recently Since capacity is increasing, it is predicted that warming of the earth arises according to greenhouse effect. A thermal power station is CO<sub>2</sub> by combustion, although the heat energy which a fossil fuel etc. is burned

and is obtained is transformed into electrical energy. In order to discharge gas so much, it is becoming difficult to build a new thermal power station. Therefore, it stores in the rechargeable battery which installed the Nighttime power which is dump power in ordinary homes as a deployment of the power made with generators, such as a thermal power station, and the so-called load leveling which equalizes a load at day ranges with much power consumption using this is proposed.

[0003] Moreover, for the application of the electric vehicle which has the description of not discharging the atmospheric pollutant containing COx, NOx, CH, etc., development of the rechargeable battery of a high energy consistency is expected. Furthermore, for the power-source application of portable devices, such as a book mold personal computer, a word processor, a video camera, and a cellular phone, development of a small, lightweight, and highly efficient rechargeable battery is pressing need.

[0004] Development of the so-called "lithium ion battery" of the rocking chair mold which used for the negative-electrode matter the carbon ingredient which can intercalate in the positive-electrode matter the above-mentioned small one and the lithium intercalation compound which is lightweight and deintercalates a lithium ion at the reaction at the time of charge as a rechargeable battery of high performance, for example between the layers of the six membered ring reticulated flat surface form by the carbon atom in a lithium ion, and which is represent by graphite progresses, and the part is put in practical use.

[0005] However, in the "lithium ion battery" mentioned above, since the negative electrode which consisted of carbon ingredients can intercalate only a maximum of 1/per C atom only of lithium atoms of 6 theoretically, the rechargeable battery of the high energy consistency which is equal to the lithium primary cell when using a metal lithium for the negative-electrode matter is unrealizable. Since a metal lithium will carry out dendritic growth and will cause a short circuit on the surface of carbon if it is going to store the lithium more than the amount of lithiums which can be temporarily inserted between the layers of the carbon of a negative electrode at the time of charge, the rechargeable battery of the high capacity which stored more than the amount of lithiums that can be inserted between layers is not realizable.

[0006] On the other hand, in the lithium cell of the high capacity which uses a lithium metal for a negative electrode, by the repeat of charge and discharge, it is easy to generate the dendrite of the lithium constituting the main cause of a short circuit, and stopping the dendritic growth of this lithium makes rechargeable battery-ization of a



lithium cell difficult rather than it is easy.

[0007] Moreover, since the lithium secondary battery which used for the negative electrode metals with which a lithium metal deposits at the time of charge, such as a lithium metal and aluminum, can also expect a high energy consistency, although it inquires, the thing with the life to a practical use field is not put in practical use.

[0008] Also with the rechargeable battery which used carbon for the negative electrode, when the dendrite of a lithium grows at a negative electrode also with the rechargeable battery using the negative electrode with which a lithium metal deposits at the time of charge and a negative electrode and a positive electrode change into a short circuit condition, by generating heat by consuming the energy which a cell has for a short time, and the solvent of the electrolytic solution decomposing, and generating gas, internal pressure increases and a cell may be damaged to an informal Noh dance. As this cure, for safety reservation of a lithium secondary battery (the rechargeable battery using the oxidation reduction reaction of a lithium ion will be generically called a lithium secondary battery below) also including the above-mentioned lithium ion battery The porous film of polyethylene or polypropylene whose melting point is 120 degrees C ~ 170 degrees C is used for the separator between a positive electrode and a negative electrode. If a cell short-circuits by a certain cause and internal temperature rises to the melting point of an ingredient, the structure which \*\*\*\*\* is closed, a separator insulates a negative electrode and a positive electrode electrically, and a cell reaction stops is tried. However, although it is an emergency safety practice, it cannot become the decisive approach of developing the life of the negative electrode in a lithium secondary battery by leaps and bounds.

[0009] Moreover, with the lithium secondary battery using the porous film which consists of an organic polymer mentioned above as a separator, with not functioning, unless the temperature of a cell becomes an elevated temperature 120 degrees C or more, and the separator with which it once fused and the hole was closed, even if temperature falls, the insulating condition between a positive electrode and a negative electrode remains, and the engine performance of a cell is not recovered. From this, high capacity-ization of a cell can be realized, and the dendritic growth of a lithium is stopped at the time of charge, and development of the means which can also develop a cycle life is desired.

[0010] Moreover, also in the rechargeable battery which consists of a nickel zinc cell and an air zinc cell, since a zincky dendrite occurred, a separator was penetrated and a zinc negative electrode and a positive

electrode short-circuited by the repeat of charge and discharge like a lithium secondary battery, there was the same problem as the lithium secondary battery mentioned above that a cycle life is short. Therefore, in the lithium secondary battery or the zinc rechargeable battery, that from which-izing can be carried out [ high capacity ] and sufficient cycle life is acquired is desired strongly.

[0011]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned trouble, and in the rechargeable battery whose negative-electrode active material is a lithium or zinc, a cycle life is long and it aims at offering the rechargeable battery of a high energy consistency.

[0012]

[Means for Solving the Problem] The rechargeable battery of this invention has an electrolyte and the movable ion which participates in a cell reaction between a negative electrode, a positive electrode, and this positive electrode and a negative electrode, and is a rechargeable battery characterized by having the layer which has the free passage hole of the aperture which can be changed according to an environment, and cell housing which holds these. In addition, "the ion which participates in a cell reaction" is ion which receives oxidation and reduction and participates in this reaction in the charge-and-discharge reaction of a rechargeable battery.

[0013] In the layer which intervenes between a positive electrode and a negative electrode, the rechargeable battery of this invention has the movable ion which participates in a cell reaction, and is characteristic at the point that the free passage hole (through tube) which has the path (width of face) which can be changed according to an environment, and passes between a positive electrode and a negative electrode exists. A "free passage hole" is a hole which opens between the positive electrode in a rechargeable battery, and a negative electrode for free passage here, and it can become the path to which the ion which participates in a cell reaction moves between positive-electrode negative electrodes through the free passage hole concerned. The path (width of face) is changed according to change of an electrical potential difference [ / near / where it between the above-mentioned positive electrode and a negative electrode exists / the location ], and temperature, and especially this free passage hole changes resistance between the positive electrode in the free passage hole concerned, and a negative electrode. For example, in a cell reaction, in the circumference of a single string through-hole, an electrical potential

difference changes so that the width of face of the free passage hole concerned may become narrow locally, when [ high and/or ] temperature is high, the resistance in near [ concerned ] a free passage hole becomes high, and advance of a cell reaction is suppressed.

[0014] At the charge reaction of a rechargeable battery, it may grow up in the shape of [ which high electric field arise locally between a positive electrode and a negative electrode, temperature rises locally, and a reaction advances too much, and was mentioned above depending on the component and reaction mechanism of a cell under the effect of the positive electrode and the negative electrode being formed in the ununiformity about the shape of surface type, or a presentation ] a negative-electrode active material dendrite, or electrolytic disassembly may arise. As a result, possibility of resulting in the short circuit between a positive electrode and a negative electrode in such a part becomes strong. Therefore, a short circuit is prevented with control of advance of a cell reaction with constituting the field between the positive electrode of a cell, and a negative electrode from a free passage hole with which width of face is changed so that resistance near the part which the above-mentioned quantity electric field or a temperature rise produces may go up.

[0015] The dendritic growth which is the cell which can expect a high energy consistency and was mentioned above is controlled, and the rechargeable battery of this invention is used as the thing (lithium secondary battery) which contains a lithium element at least in the negative electrode at the time of charge preferably, or a thing (zinc rechargeable battery) which contains a zinc element at least.

[0016] In the rechargeable battery of this invention, what the layer between said positive electrode and a negative electrode has pore, has the poly membrane to which it is the part where field strength is higher than a perimeter, and the pole diameter decreases, or pore, and becomes from the poly membrane to which a temperature rise is a large part and the pole diameter decreases from a perimeter is desirable.

[0017] It is desirable that the above-mentioned poly membrane consists of complex of a polymer liquid crystal, or a macromolecule and liquid crystal at least, and --- the relaxation time to which the electrical potential difference is not impressed for the liquid crystal section of the poly membrane --- a negative-electrode flat surface --- perpendicular orientation --- or --- if inclination orientation is carried out, and high electric field are locally impressed in the part from which the dendritic growth of an active material tends to happen at the time of charge or a temperature rise happens --- a negative-electrode flat

surface -- parallel orientation -- or -- being disorderly (random) -- it is desirable to carry out orientation and to decrease the negative-electrode flat-surface lay length (pole diameter) of the pore section. It is desirable that the polymer liquid crystal or liquid crystal of a poly membrane consists of liquid crystal which has a negative dielectric anisotropy at least.

[0018] Moreover, it is desirable that the above-mentioned poly membrane consists of polymer gels at least.

[0019] When this invention person investigated minutely the part and the conditions that growth of the dendrite of a lithium took place at the time of the charge of a lithium secondary battery which used a metal lithium, aluminum, and a carbon ingredient for the negative electrode, the part as for which a lithium tends to carry out dendrite (arborescence) growth is a part where field strength, such as a height on the front face of a negative electrode, is high, and the big current found it out flowing and being exoergic. The same view was acquired also in the nickel zinc rechargeable battery and air zinc cell which used zinc for the negative electrode. It checks raising resistance of the above-mentioned part alternatively, and that the dendritic growth of a lithium or zinc is controlled based on this knowledge at the time of a header and charge.

[0020] With the rechargeable battery of this invention, in the rechargeable battery of a lithium or zinc, a negative-electrode active material is equipped with the layer which consists of a part where field strength, such as a height on the front face of a negative electrode, is high, and/or a free passage hole with which the aperture of the free passage hole between negative-electrode positive electrodes becomes narrow locally in the part where a temperature rise is intense, raises resistance with the free passage hole concerned, and prevents a short circuit. In this way, it can stop that a lithium or zinc grows in the shape of a dendrite at the time of charge, consequently the cycle life at the time of charge and discharge can be developed by leaps and bounds. Therefore, thereby, the rechargeable battery of the long high energy consistency of a cycle life is realizable.

[0021] In addition, in this invention, as long as an "active material" is matter which participates in the electrochemical reversible reaction (manipulate return) of the charge and discharge in a cell and it is the matter which participates in the above-mentioned reaction in person further, the matter holding other matter which participates in the above-mentioned reaction is also included. In addition, in a lithium secondary battery, as a negative-electrode active material, it is held

at a negative-electrode side at the time of charge, and at the time of discharge, a lithium dissolves into the electrolytic solution and serves as a lithium ion. Moreover, in a zinc rechargeable battery, as a negative-electrode active material, it is at the discharge time, and zinc reacts with a hydroxide ion and changes to zinc hydroxide or a zinc oxide.

[0022]

[Embodiment of the Invention] Hereafter, the example of an embodiment of this invention is explained with reference to drawing 1, drawing 2, and drawing 5. Drawing 1 is the conceptual diagram showing the cross section of an example of the rechargeable battery of this invention. The rechargeable battery of this invention shown in this drawing 1 a negative electrode 101 It counters with a positive electrode 102 through the separator 103 which makes an electrolyte serve a double purpose or it held the electrolytic solution. And the ion which participates in the cell reaction which is the description of this invention is movable between the negative electrodes 101 and positive electrodes 102 which counter, and have the free passage hole of the aperture which can be changed according to an environment. The structure in which the porous poly membrane 100 which has pore was formed as a layer which has the free passage hole with which a path (width of face) becomes small in the field where especially electrolysis reinforcement and temperature are high, and resistance becomes high is held in the cell housing 104. In the place where the place and temperature to which high electric field are impressed rose although the porous poly membrane 100 could pass the ion accompanying a cell reaction, it changes so that transparency of the metal which pore narrows, and passage of the ion accompanying a cell reaction is controlled, and deposits at the time of charge may be restricted, and it has the function in which resistance increases. In addition, the positive-electrode terminal 106 linked to a positive electrode 102 and the negative-electrode terminal 105 linked to a negative electrode 101 are respectively pulled out out of housing 104.

[0023] This function is explained using drawing 5. Drawing 5 is a conceptual diagram explaining the function of the rechargeable battery of this invention, and is an example in the case of connecting DC power supply to the rechargeable battery of this invention of drawing 1, and charging it. When the electric-field concentration section 107 which is the part where field strength like a projection is high exists in the negative-electrode front face of the rechargeable battery of drawing 1, In this electric-field concentration section 107, high electric field are impressed from the circumference, therefore current density becomes

high and generate heat. Pore is narrowed in the part 108 where the high electric field of a poly membrane 100 are impressed, and temperature rises then, and resistance goes up. In the electric-field concentration section 107 of the part where the high electric field on the front face of a negative electrode are impressed as a result, a deposit of a dendrite-like negative-electrode active material will be suppressed at the time of charge, and the internal short circuit between a negative electrode and a positive electrode will be suppressed.

[0024] Drawing 2 is the conceptual diagram showing the example of arrangement of the poly membrane which are the negative electrode in the rechargeable battery of this invention, a positive electrode, a separator, and a means to prevent the dendritic growth of a negative-electrode active material. (a) of drawing 2, (b), and (c) show the negative electrode 101 in the cross section of the rechargeable battery of drawing 1, a positive electrode 102, a separator and the electrolytic solution 103, and the example of arrangement of the porous poly membrane 100 respectively. In (a) of drawing 2, the above-mentioned poly membrane 100 is the example established between the negative electrode 101 and the separator 103. In (b) of drawing 2, the above-mentioned poly membrane 100 is the example established between the positive electrode 102 and the separator 103. In (c) of drawing 2, it is the example in which the above-mentioned poly membrane 100 made the separator 103 serve a double purpose, and was prepared between the negative electrode 101 and the positive electrode 102.

[0025] Although the rechargeable battery of this invention has a porous poly membrane and an electrolyte on the layer and concrete target which have a free passage hole which was mentioned above at least between the positive electrode, the negative electrode, the positive electrode, and the negative electrode and has a separator and cell housing further, it explains each component below.

[0026] (Poly membrane) Prepare between the negative electrode which constitutes the rechargeable battery which is the description of this invention, and a positive electrode. It is the field layer which consists of a free passage hole which is movable as for the ion which participates in a cell reaction, and has the path (width of face) which can be changed according to an environment. In order to prevent the dendritic growth of the negative-electrode active material at the time of charge as a function of a poly membrane (at the example shown by drawing 1, it is the film 100) porous as a layer If it has the pore which penetrates the ion which participates in a cell reaction, and high electric field are impressed or temperature rises, it is required to

have the property that the pore diameter narrows.

[0027] As the quality of the material of a poly membrane, the composite of a liquid crystal macromolecule, a base material and the macromolecule which changes, and liquid crystal, and polymer gel can be used, for example. As liquid crystal of the composite of the liquid crystal macromolecule of the ingredient of the above-mentioned poly membrane or a base material, the macromolecule that changes, and liquid crystal, when electric field are impressed, the liquid crystal with which the major axis of a molecule is located in a line with electric field and a perpendicular is desirable, and the liquid crystal whose dielectric anisotropy is negative is more desirable. When the major axis of the molecule of the liquid crystal part of a poly membrane is located in a line with electric field and a perpendicular direction, the pore (free passage hole mentioned above) penetrated in the direction of electric field will be narrowed. Moreover, in the polymer gel which forms the above-mentioned poly membrane, it is preferably required for 20% or more of big cubical expansion to happen by the temperature rise. The pore in polymer gel will be narrowed by cubical expansion.

[0028] Furthermore, when preparing this polymer gel in a negative-electrode side, it is desirable that it is the cationic polymer gel which has positive charge. In order that a lithium cation may maintain an assembly and neutralization conditions near the negative-electrode front face at the time of charge, cationic polymer gel lengthens a molecule and expands. When preparing this polymer gel in a positive-electrode side, it is desirable that it is the anionic polymer gel which has negative charge. In order that an anion may maintain an assembly and neutralization conditions near the positive-electrode front face at the time of charge, anionic polymer gel lengthens a molecule and expands.

[0029] The negative-electrode active material which deposits at the time of the ion contributed to a cell reaction or charge can prevent penetrating the pore of a poly membrane and a separator, and even a positive electrode reaching and carrying out an internal short circuit by being narrowed, as mentioned above when high electric field arise locally [ the pore of the characteristic poly membrane which constitutes the rechargeable battery of this invention ] near [ this ] pore, or when a temperature rise arises.

[0030] In addition, 1 micrometer or less is usually preferably made into 2-1000Å that what is necessary is just the magnitude which penetrates the ion which participates in a cell reaction as magnitude of the path of the pore formed in a poly membrane.

[0031] Moreover, it is [ that what is necessary is just the range where



the function for raising resistance in case ion moves is obtained ] usually preferably [ 20 - 98% of ] desirable [ the contraction rate of the path of the pore ], although the pore diameter will narrow if high electric field are impressed or, as for the pore of a poly membrane, temperature rises 10% or more as a ratio to the original contracted pore diameter.

[0032] In adopting as a lithium secondary battery especially a poly membrane that was mentioned above, before including in a cell at least and pouring in the electrolytic solution, it is necessary to remove moisture enough by approaches, such as reduced pressure drying, about the film concerned. Supposing dehydration was not fully performed, the lithium which deposits at the time of charge, and this moisture will react, lithium compounds, such as a lithium hydroxide which cannot be used at the time of discharge, will be formed, and the fall of discharge quantity of electricity will be brought about.

[0033] As an approach of forming the porous poly membrane which has the above-mentioned free passage hole using a polymer liquid crystal ingredient, film formation is carried out by the casting method, or the solution which dissolved the polymer liquid crystal ingredient in the solvent is applied to a direct negative electrode, a separator, and a positive-electrode front face, and the film is formed. Subsequently, it dries, a solvent is removed and pore is formed. It is also possible to form a poly membrane in a polymerization reaction and coincidence using the monomer from which it forms using a polymer liquid crystal ingredient, and also a polymer liquid crystal is obtained at a polymerization reaction. Moreover, in order to adjust pore distribution depending on the case, at the time of film formation, an electrolyte etc. is added, for example, film formation is carried out, extract removal of the matter which can carry out extract removal and which was further added after desiccation at the time of film preparation is carried out, and pore distribution is adjusted.

[0034] After adding the matter from which the back is removable as the preparation approach of pore so that it may grow into a porosity rate [ \*\*\*\* / at the time of poly membrane formation ], a solvent is added if needed, the matter removable to the time of film formation or the back is removed, and pore is prepared. As removable matter, the electrolyte and organic solvent which can be eluted and which are used, for example for the electrolytic solution are mentioned. When it uses for the quality of an additive which can remove an electrolyte, there is little effect which it has on a cell property. It is also possible to use the low solvent of the boiling point mixed with the solvent which is made to

evaporate or disassemble, and removes under heating or reduced pressure as matter in which another removal is possible, or is removed to homogeneity.

[0035] Since the dissolution stability over the electrolytic solution is increased after film formation, it is desirable to cause crosslinking reaction and to also make it construct a bridge. Or it adds a cross linking agent at the time of film formation and causes crosslinking reaction as the bridge formation approach, the method of irradiating ultraviolet rays and a radiation after film formation, and causing crosslinking reaction is mentioned.

[0036] As an approach of forming the porous poly membrane which has the above-mentioned free passage hole with the complex of polymeric materials and a liquid crystal ingredient By the casting method which casts on the flat and uniform metal base material which mixes a liquid crystal ingredient to the polymer solution which dissolved the macromolecule used as a base material in the solvent, and rotates the obtained mixed solution, and is film-ized Or it applies to a direct negative electrode, a separator, or a positive-electrode front face, and the film is formed, it dries, a solvent is removed, and a poly membrane is prepared. It is also possible to add quality of an additive, for example like an electrolyte which can remove the back depending on the case, and to perform poly membrane formation like above-mentioned polymer liquid crystal film formation, for adjustment of pore distribution. Furthermore, since causing crosslinking reaction and also making it construct a bridge after film formation increases the stability over the electrolytic solution, it is desirable. As the bridge formation approach, the bridge formation approach of the above-mentioned polymer liquid crystal film and the same approach are employable.

[0037] As for the liquid crystal of the bipolar membrane of the above-mentioned polymer liquid crystal film and macromolecule which are a poly membrane, and liquid crystal used as a layer field which has the free passage hole which can be changed for a hole (width of face) according to the environment between a positive electrode and a negative electrode, in the rechargeable battery of this invention, it is desirable to make a negative-electrode electrode flat surface carry out perpendicular orientation or inclination orientation at the time of film formation.

[0038] As the orientation approach, a perpendicular direction, an inclination, or the approach of impressing in parallel can be used for a negative-electrode electrode flat surface for a magnetic field or electric field before the above-mentioned poly membrane solidification. It is controlled by selection of stress impression, the orientation

processing on the front face of a base which forms the film, heating or cooling, the optimal solvent, and optimum density etc. as the other orientation approaches.

[0039] As an example of the orientation processing on the front face of a base which forms the above-mentioned film, the chemisorption of organic metal coupling agents, such as physical adsorption of amphipatic molecules, such as p-(octyloxy)-p'-hydroxy azo BENZENE, a dimethyl hexadecyl ammonium star's picture, N-[11-BUROMO undeca noil]-L-glutamic acid didodecyl ester, a hexadecyl tributyl phosphonium star's picture, a stearyl tributyl phosphonium star's picture, lecithin, and a cetyl trimethylammonium star's picture, and sterile trichlorosilan, is mentioned as an art of perpendicular orientation.

[0040] The approach of carrying out the slanting vacuum evaporations of a metal or the organic giant molecule by the vacuum deposition approaches, such as sputtering and electron beam evaporation, and forming the orientation film in a base front face as inclination orientation, is mentioned.

[0041] As an approach of on the other hand forming the porous poly membrane which has the above-mentioned free passage hole by polymer gel material (a) [ whether polymer gel is formed by direct polymerization and crosslinking reaction from a monomer, and ] [ whether after a separator is immersed into (b) monomer solution which forms lifting polymer gel for crosslinking reaction after forming a macromolecule, polymer gel is formed by crosslinking reaction, and ] After a separator is immersed into a polymer solution, form lifting polymer gel for crosslinking reaction. (c) After forming polymer gel powder by the polymerization and crosslinking reaction from a monomer, into a polymer solution, distribute polymer gel powder, and solidify and form. (d) After casting a polymer solution on a negative-electrode front face, a positive-electrode front face, or a separator front face, lifting polymer gel is formed for the postpolymerization reaction and crosslinking reaction which formed polymer gel in crosslinking reaction, or cast the monomer solution. The thickness of polymer gel is adjusted at the time of the formation at the time of a polymerization or bridge formation, is used as it is, or it dries after formation, and it adjusts and uses thickness for homogeneity by press working of sheet metal etc. The thickness of polymer gel can be adjusted in the depth of the solvent kind at the time of formation, and a concentration and a reaction container etc. The expansion coefficients of polymer gel are a monomer kind, polymerization degree, a degree of cross linking, the class of solvent and concentration, the electrolytic concentration contained in a

solvent, and can be adjusted.

[0042] As an approach of producing as a film or a sheet, the porous poly membrane formed of the complex of the polymer liquid crystal which others mentioned above, and a macromolecule and liquid crystal, or polymer gel Besides the casting method (the solution casting method) which casts on the flat and uniform metal base material turning around the polymer solution which dissolved with the solvent, and is film-ized The extrusion method (melting extrusion method) which extrudes and film-izes the giant-molecule liquid fused with heat from T mold dice, and the calender method which rolls out and film-izes a high polymer between the rolls of two or more can be used. By the extrusion method, after using and film-izing the macromolecule before bridge formation, crosslinking reaction is caused, and a high polymer film is obtained. By the calender method, a film is produced using the dry macromolecule.

[0043] (Liquid crystal ingredient) The rye OTORO pick ingredient in which liquid crystallinity is shown for a liquid crystal layer under existence of a \*\*\*\* thermotropic ingredient and a solvent, for example through a fusion process as a liquid crystal ingredient used for the complex of the macromolecule organic liquid crystal used as the ingredient of a porous poly membrane mentioned above, or a macromolecule and liquid crystal is also included. Although a nematic liquid crystal, KORESU tic liquid crystal, SUMECHIKKU liquid crystal, disco tic liquid crystal, the strong dielectric liquid crystal in which spontaneous polarization is shown are mentioned as a class of orientation of the liquid crystal used, it is desirable that it is the liquid crystal in which a negative dielectric anisotropy is shown, and it is more desirable that a nematic liquid crystal phase or a KORESU tic liquid crystal phase is shown.

[0044] moreover -- the relaxation time to which the electrical potential difference is not impressed -- a negative-electrode flat surface -- the liquid crystal section -- perpendicular orientation -- or the part from which the dendritic growth of the active material with which inclination orientation is carried out, high electric field are locally impressed at the time of charge, and a temperature rise happens tends to happen -- a negative-electrode flat surface -- parallel orientation -- or it is more desirable to carry out orientation disorderly.

[0045] Furthermore, it is desirable to blend and use two or more liquid crystal so that it may function according to the service temperature of a rechargeable battery. As for the above-mentioned liquid crystal, it is desirable that orientation processing perpendicular to a negative-electrode flat surface or inclination orientation processing of a

rechargeable battery is performed, and orientation (they are a perpendicular or inclination orientation to a negative-electrode side) of the above-mentioned liquid crystal in an initial state is given. The tilt angle to the negative-electrode flat surface of the liquid crystal molecule in the initial state by these orientation processings is 45 degrees or more.

[0046] As a liquid crystal ingredient in which the above-mentioned negative dielectric anisotropy used for this invention is shown 2, 3-JIFURORO benzene derivative, a pyridazine derivative, a fluorination hydroquinone cyclohexane-carboxylic-acid ester compound, A fluorination tolan compound, a cyanobenzene carboxylate compound, A cyanogen cyclohexane compound etc. is mentioned. Also in it 3, 6-2 permutation -1, 2-dicyano benzens, 3, 6-2 permutation pyridazine, 3, 6-2 permutation -1, 2-JIFURORO benzens, 3, 6-2 permutation-1-cyanobenzene, 1, and 4-2 permutation-1-cyano cyclohexanes are mentioned as an example which shows a negative, comparatively big dielectric anisotropy.

[0047] The structure of the above-mentioned liquid crystal macromolecule used for this invention has the principal chain form polymer which the MESOGEN radical which is the group of a linearity conjugation form, or a MESOGEN radical, an alkyl chain or an oxyethylene chain combined linearly by turns, and the side-chain form polymer which the MESOGEN radical combined with the principal chain as a side chain through the direct or alkyl chain. As the above-mentioned MESOGEN radical, a benzylidene aniline, an azobenzene, azoxybenzene, a stilbene, phenyl benzoate, a benzoyl aniline, a biphenyl, a benzylidene acetophenone, a benzylidene azine, etc. are mentioned.

[0048] (Macromolecule in macromolecule-liquid crystal complex) As polymeric materials used as the macromolecule used as the porous poly membrane mentioned above, and the solid-state in the complex of liquid crystal, insoluble polymeric materials and the polymeric materials which were made to construct a bridge and were made insoluble at the electrolytic solution can be used for the electrolytic solution of a cell. Furthermore, a meltable organic macromolecule or its raw material monomer can be used for the solvent used for preparation of macromolecule-liquid crystal complex (when a monomer is used, a polymerization is carried out in the preparation phase of complex). As an example of the above-mentioned polymeric materials, polyolefines, such as polyethylene and polypropylene, a fluororesin, a polyvinyl chloride, polyvinyl alcohol, polyacrylamide, polyester, a polyamide, polyethylene oxide, etc. are mentioned.

[0049] (Polymer gel) In this invention, what inhales the macromolecule

or solvent which constitutes the internal short circuit prevention means of a lithium secondary battery preferably as polymer gel used as the ingredient of a porous poly membrane mentioned above, and which has the insoluble three-dimensional network in the solvent, and is in a swelling condition is used.

[0050] As this polymer gel, for example Polyacrylamide, N, and N-diethyl acrylamide polymer, N-isopropyl acrylamide polymer, an N-isopropyl acrylamide-acrylic-acid sodium copolymer, An N and N-diethyl acrylamide-acrylic-acid sodium copolymer, An acrylamide-(methacrylamide propyl) trimethylammonium chloride copolymer, An acrylamide-TORIMECHIRU (N-acryloyl-3-aminopropyl) ammonium iodide copolymer, A polystyrene and styrene-styrene SARUFONETO copolymer, polyvinyl methyl ether, Polyvinyl alcohol-polyacrylic acid compound gel, polyacrylic acid, polymethacrylic acid, and methacrylic-acid-2-hydroxyethyl, a cellulose, a polyethylene glycol, polyethylene oxide, polyvinyl alcohol, etc. are mentioned. Polymer gel with ionic dissociation radicals, such as an N-isopropyl acrylamide-acrylic-acid sodium copolymer, N, and N-diethyl acrylamide-acrylic-acid sodium copolymer, an acrylamide-(methacrylamide propyl) trimethylammonium chloride copolymer, an acrylamide-TORIMECHIRU (N-acryloyl-3-aminopropyl) ammonium iodide copolymer, and a styrene-styrene SARUFONETO copolymer, is used preferably among these. Moreover, since polymer gel like polyacrylamide [ which is in the condition which the giant-molecule chain contracted in ordinary temperature among the above-mentioned polymer gels ], N, and N-diethyl acrylamide polymer also expands at an elevated temperature, it is desirable although it is used for this invention.

[0051] as the formation approach of polymer gel usable at this invention -- a chemical bond -- or what is depended on intermolecular association is adopted. As an approach of forming gel by the chemical bond, there are an approach of constructing a bridge over polymerization reaction time and the approach of constructing a bridge after a polymerization, and there are bridge formation by hydrogen bond, bridge formation by ionic bond, and bridge formation by coordinate bond as an approach of constructing a bridge in between macromolecule chains by association between molecules.

[0052] Moreover, or energy, such as formation of the bridged structure by the polycondensation of for example, a divinyl compound or a polyfunctional compound, heat, light, a radiation, and plasma, performs a polymerization and a bridging to coincidence, after compounding a straight chain-like macromolecule, there is also the approach of carrying out a bridging among the approaches by bridge formation.

[0053] As an approach of carrying out a bridging to polymerization reaction time, photopolymerization which irradiates the polymerization according ethylene glycol dimethacrylate and methylenebis acrylamide to a radical initiator, the radiation polymerization which irradiates a gamma ray and an electron ray, and the light which is in agreement with the absorption wavelength of a vinyl monomer under crosslinking agent existence as a crosslinking agent, or adds a photosensitizer and carries out an optical exposure is mentioned, for example. .

[0054] As an approach of carrying out the bridging of between giant-molecule chains later, the cellulose and polyvinyl alcohol which have a hydroxyl group, for example An aldehyde, Construct a bridge by chemical reactions, such as N-methylol compound, dicarboxylic acid, and bis-EPO SHIKIDO. How to gel the giant molecule which has amino acid by the aldehyde or the glycidyl group, How to construct a bridge underwater in polyvinyl alcohol or the polymethyl vinyl ether by radiation irradiation, such as a gamma ray, Polyvinyl alcohol and N-vinyl pyrrolidone Diazo resin, bis-azide, The approach of carrying out photodimerization of the polymer which has sensitization radicals, such as a still BAZORIUMU salt, in water soluble polymers which carry out a bridging by optical crosslinking agents, such as dichromate, such as polyvinyl alcohol, and the approach of contacting the plasma generated by gaseous discharge to macromolecule material, and carrying out a bridging are mentioned.

[0055] Gel can be formed by the hydrogen bond and ionic bond between macromolecules, chelate formation, etc., and gel can be formed by making hydrogen bond form between macromolecules by the freezing vacuum-drying method, the freezing thawing method, etc., and mixing two kinds of different macromolecules like polymethacrylic acid, a polyethylene glycol and polyacrylic acid, and polyvinyl alcohol. The poly ion complex gel can be formed by mixing the poly anions, such as the poly cations, such as polyvinylbenzyl trimethylammonium, and sodium polystyrene sulfonate. It can be made to be able to combine with alkali and alkaline earth metal, and strong acid nature polymers, such as polycarboxylic acid, such as polyacrylic acid, and polystyrene sulfonate, can form gel.

[0056] (Negative electrode) What the thing containing a lithium element is preferably used at the time of charge as an ingredient of the negative-electrode ingredient (it is a negative electrode 101 at the example shown in drawing 1 ) in the rechargeable battery of this invention (lithium secondary battery), or contains a zinc element is used (zinc rechargeable battery). The negative electrode is obtained by fabricating a negative-electrode ingredient on a charge collector preferably.



[0057] As a negative-electrode ingredient for lithium secondary batteries, a lithium metal, a carbon material including a graphite, a metallic material, and the ingredient that a lithium like a transition-metals compound intercalates are mentioned, for example. Metals, such as nickel of the porosity which has the pore which contains a lithium, and metallic materials, such as aluminum which forms an alloy, and the lithium which deposits as the above-mentioned metallic material, and serves also as a charge collector, etc. are suitable.

[0058] If it is a foil and tabular as a configuration of the above-mentioned charge of negative-electrode material, it can use as it is. Moreover, if powdered, a binder will be mixed, an electric conduction nominal member is also added depending on the case, a paint film is formed on a charge collector, and a negative electrode is created. Moreover, plating and vacuum deposition can also be used as an approach of forming the thin film of the above-mentioned ingredient on a charge collector. As the above-mentioned vacuum evaporation approach, approaches, such as CVD (Chemical Vapor Deposition), electron beam evaporation, and sputtering, are mentioned. It is required to also fully dry the negative electrode for which lithium secondary batteries under reduced pressure.

[0059] What mixed the binder as a negative electrode for zinc rechargeable batteries into the thing, zinc-oxide powder or zinc powder in which the zincky plating film or the zincky vacuum evaporation film was formed on a zincky foil and a zincky plate, and the charge collector, and zinc-oxide powder, and formed the paint film on the charge collector (adding an electric conduction nominal member depending on the case) can be used for a negative electrode.

[0060] (Positive electrode) The positive electrode (at the example shown in drawing 1, it is a positive electrode 102) in the rechargeable battery of this invention consists of ingredients, such as a charge collector, positive active material, an electric conduction nominal member, and a binder. This positive electrode fabricates what mixed positive active material, the electric conduction nominal member, the binder, etc. on the front face of a charge collector, and is produced.

[0061] As an electric conduction nominal member used for a positive electrode, metal impalpable powder, such as carbon black, such as a graphite, KETCHIEN black, and acetylene black, and nickel, etc. is mentioned.

[0062] As a binder used for a positive electrode, when a fluororesin like [ when the electrolytic solution is a non-aqueous-solvent system ] polyolefines, such as polyethylene and polypropylene, or polyvinylidene

fluoride and a tetrafluoroethylene polymer, and the electrolytic solution are water-solution systems, polyvinyl alcohol, a cellulose, or a polyamide is mentioned, for example.

[0063] Generally in the lithium secondary battery whose negative-electrode active material is a lithium, transition-metals oxide, a transition-metals sulfide, lithium-transition-metals oxide, or a lithium-transition-metals sulfide is used as positive active material. Sc and Y which are the element which has d husks or f husks partially as a transition-metals element of a transition-metals oxide or a transition-metals sulfide, for example, a lanthanoids, actinoid one, and Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, Pt, Cu, Ag and Au are mentioned. Especially, Ti, V, Cr, Mn, Fe, Co, nickel, and Cu which are the first sere metal are used suitably.

[0064] In the nickel zinc rechargeable battery whose negative-electrode active material is zinc, oxidation nickel hydroxide is used as positive active material.

[0065] The positive electrode is constituted from the charge collector, the catalyst, and the repellent by the air zinc rechargeable battery whose negative-electrode active material is zinc, using oxygen as positive active material. As a catalyst, porous carbon, porosity nickel, copper oxide, and nickel oxide are used, for example. As a repellent, a porous tetrafluoroethylene polymer and a fluororesin like Pori fluoride kinky thread NIDEN are used. In the zinc bromine rechargeable battery whose negative-electrode active material is zinc, a bromine is used as positive active material.

[0066] (Charge collector of a negative electrode and a positive electrode) the charge collector used with the negative electrode and positive electrode in a rechargeable battery of this invention supplies efficiently the current consumed by the electrode reaction at the time of charge and discharge — it is — it is — the duty which collects the current to generate is borne. Therefore, the quality of the material with it is desirable. [ high and electric conductivity and ] [ inactive to a cell reaction as an ingredient which forms the charge collector of a negative electrode and a positive electrode ]

[0067] As the desirable quality of the material, nickel, titanium, copper, aluminum, stainless steel, platinum, palladium, gold, zinc, various alloys, and two or more sorts of compound metals of the above-mentioned ingredient are mentioned. As a configuration of a charge collector, letters of formation, such as the shape of the shape of the shape of tabular and a foil and a mesh and sponge, fibrous, a punching metal, and an expanded metal, are employable, for example.

[0068] (Separator) The separator (at the example shown in drawing 1 , it is 103) in the rechargeable battery of this invention is arranged between a negative electrode and a positive electrode, and has the role which prevents these short circuits. Moreover, it may have a role holding the electrolytic solution.

[0069] a lithium ion or a hydroxide ion has the pore which can move, and a separator's is insoluble to the electrolytic solution, and stable --- required --- certain \*\* Therefore, as a separator, the ingredient of nonwoven fabrics, such as polyolefines, such as glass, polypropylene, and polyester, a fluororesin, and a polyamide, or micropore structure is used suitably, for example.

[0070] Moreover, the metallic-oxide film which has micropore, or the resin film which compound-ized the metallic oxide can also be used. Since it is hard to penetrate a dendrite when the metallic-oxide film which has the structure multilayered especially is used, effectiveness is in short circuit prevention. When the fluororesin film which is a fire retarding material, the glass which is an incombustible material, or a metallic-oxide film is used, safety can be raised more.

[0071] (Electrolyte) The ion which participates in the cell reaction mentioned above is movable, and the electrolyte in the rechargeable battery of this invention is held at the layer (at the example shown in drawing 1 , it is the poly membrane 100) and separator 103 which have the free passage hole which has the path which can be changed according to environments, such as an electrical potential difference or temperature. The following three kinds are mentioned as a usage of this electrolyte.

- (1) How to use in the condition as it is.
- (2) How to use as a solution which dissolved in the solvent.
- (3) How to use as what was fixed by adding gelling agents, such as a polymer, in a solution.

[0072] Generally, it is used for it, making a solvent carry out liquid retaining of the electrolytic solution which melted the electrolyte to a porous separator. Electrolytic conductivity needs to be  $5 \times 10^{-3}$  or more S/cm more preferably  $1 \times 10^{-3}$  S/cm or more than cm preferably as a value in 25 degrees C.

[0073] In the lithium cell whose negative-electrode active material is a lithium, the electrolyte shown below and its solvent are used suitably. As an electrolyte, acids, such as  $H_2SO_4$ , and  $HCl$ ,  $HNO_3$ , the salts which consist of a lithium ion ( $Li^+$ ) and Lewis acid ion ( $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $ClO_4^-$ ,  $CF_3SO_3^-$ ,  $BPh_4^-$  (Ph: phenyl group)), and such mixed salt are mentioned, for example. Moreover, the salt which consists of cations,

such as sodium ion, potassium ion, and tetra-alkylammonium ion, and Lewis acid ion can also be used. As for the above-mentioned salt, it is desirable to heat under reduced pressure and to perform sufficient dehydration and deoxidation.

[0074] As an electrolytic solvent, for example An acetonitrile, a benzonitrile, Propylene carbonate, ethylene carbonate, dimethyl carbonate, Diethyl carbonate, dimethylformamide, a tetrahydrofuran, A nitrobenzene, a dichloroethane, diethoxy ethane, 1, 2-dimethoxyethane, A chlorobenzene, gamma-butyrolactone, dioxolane, a sulfolane, Nitromethane, dimethyl sulfide, dimethyl ape oxide, methyl formate, 3-methyl-2-OKIDAZORIJINON, 2-methyl tetrahydrofuran, 3-propyl sydnone, sulfur dioxide, a phosphoryl chloride, a thionyl chloride, sulfuryl chlorides, or these mixed liquor can be used.

[0075] The above-mentioned solvent is good to dehydrate with an activated alumina, a molecular sieve, a phosphorus pentaoxide, a calcium chloride, etc., or to distill under alkali-metal coexistence in inert gas depending on a solvent, and to also perform impurity removal and dehydration.

[0076] Gelling is desirable in order to prevent leakage of the electrolytic solution. It is desirable to use a polymer which absorbs and swells the solvent of the electrolytic solution as a gelling agent. Polyethylene oxide, polyvinyl alcohol, polyacrylamide, etc. are used as such a polymer.

[0077] By the nickel zinc cell whose negative-electrode active material is zinc, or the air zinc cell, the electrolyte shown below is used suitably. Water is used for an electrolytic solvent. As an electrolyte, alkali (a potassium hydroxide, a sodium hydroxide, lithium hydroxide, etc.) is used, for example. Salts, such as a zinc bromide, are used by the bromine zinc cell whose negative-electrode active material is zinc.

[0078] Gelling is desirable in order to prevent leakage of the electrolytic solution. It is desirable to use a polymer which absorbs and swells the solvent of the electrolytic solution as a gelling agent. As such a polymer, polymers, such as polyethylene oxide, polyvinyl alcohol, and polyacrylamide, and starch are used, for example.

[0079] (The configuration and structure of a cell) As a concrete configuration of the rechargeable battery of this invention, there are a flat form, a cylindrical shape, a rectangular parallelepiped form, a sheet form, etc., for example. Moreover, as structure of a cell, there are a monolayer type, a multilayer type, a spiral type, etc., for example. Also in it, by winding on both sides of a separator between a negative electrode and a positive electrode, the cell of a spiral type

cylindrical shape can enlarge an electrode surface product, and has the description that a high current can be passed at the time of charge and discharge. Moreover, the cell of a rectangular parallelepiped form or a sheet form has the description which can use effectively the storage space of the device which contains and constitutes two or more cells.

[0080] Below, with reference to drawing 3 and drawing 4, more detailed explanation is given about the configuration and structure of a cell.

Drawing 3 is the sectional view of a monolayer type flat form (coin form) cell, and drawing 4 expresses the sectional view of a spiral type cylindrical shape cell. These are the same configurations as drawing 1 fundamentally, and have a negative electrode, a positive electrode, an electrolyte and a separator, cell housing, and an output terminal.

[0081] In drawing 3 and drawing 4 301 and 402 A negative electrode (a negative electrode 402 consists of a negative-electrode charge collector 400 and an active material layer 401), 303 and 408 A positive electrode (a positive electrode 408 consists of a positive-electrode charge collector 404 and an active material layer 403), 305 and 405 --- a negative-electrode terminal (negative-electrode cap), and 306 and 406 --- for a gasket and 411, as for a negative-electrode lead and 413, an electric insulating plate and 412 are [ a separator and the electrolytic solution, and 310 and 410 / a positive-electrode terminal (positive-electrode can), and 307 and 407 / a positive-electrode lead and 414 ] relief valves.

[0082] In the rechargeable battery of the flat mold (coin mold) shown in drawing 3 The laminating of the positive electrode 303 containing a positive-active-material layer and the negative electrode 301 equipped with the negative-electrode ingredient layer is carried out through the poly membrane 315 as a layer which has the separator 307 which held the electrolytic solution at least, and a free passage hole which was further mentioned above. This layered product is held from a positive-electrode side in the positive-electrode can 306 as a positive-electrode terminal, and the negative-electrode side is covered with the negative-electrode cap 305 as a negative-electrode terminal. And the gasket 310 is arranged at other parts in a positive-electrode can.

[0083] In the spiral type cylindrical rechargeable battery shown in drawing 4 The positive electrode which has the positive-electrode (active material) layer 403 formed on the positive-electrode charge collector 404, The negative electrode 402 with the negative-electrode (active material) layer 401 formed on the negative-electrode charge collector 400 It counters through the poly membrane 415 as a layer which has the separator 407 which held the electrolytic solution at least, and

a free passage hole which was further mentioned above, and the layered product of the cylindrical structure wound around multiplex is formed. The layered product of the cylindrical structure concerned is held in the positive-electrode can 406 as a positive-electrode terminal. Moreover, the negative-electrode cap 405 as a negative-electrode terminal is formed in the opening side of the positive-electrode can 406 concerned, and the gasket 410 is arranged in other parts in a negative-electrode can. The layered product of the electrode of cylindrical structure is separated from the interior of a positive-electrode can and a negative-electrode cap through the electric insulating plate 411. About the positive electrode 408, it connects with the positive-electrode can 406 through the positive-electrode lead 413. Moreover, about the negative electrode 402, it connects with the negative-electrode cap 405 through the negative-electrode lead 412. The relief valve 414 for adjusting the internal pressure inside a cell is formed in the negative-electrode cap side.

[0084] Below, an example of an approach to assemble the cell shown in drawing 3 or drawing 4 is explained.

(1) Between the negative-electrode layer (301 401) covered with the poly membrane (315 415), and the fabricated positive-electrode layer (303 403), insert a separator (307 407) and include in a positive-electrode can (306 406).

(2) Assemble a negative-electrode cap (305 405) and a gasket (310 410) after pouring in an electrolyte.

(3) A cell completes the above (2) by caulking \*\*\*\*\*.

[0085] In addition, as for ingredient preparation of the lithium cell mentioned above and the assembly of a cell, it is desirable to carry out in the dry air from which moisture was removed enough, or desiccation inert gas.

[0086] The mode of the member in the example of the rechargeable battery mentioned above is explained.

(Gasket) As an ingredient of a gasket (310 410), polyolefin resin, a fluororesin, polyamide resin, polysulfone resin, and various rubber can be used, for example. As the obturation approach of a cell, approaches, such as the glass sealed tube, adhesives, welding, and soldering, are used like drawing 3 and drawing 4 besides the "caulking" using a gasket. Moreover, various organic resin ingredients and the ceramics are used as an ingredient of the electric insulating plate (411) of drawing 4.

[0087] (Cell housing / positive-electrode can, negative-electrode cap) As cell housing which holds each part material with the rechargeable battery of this invention, each electrode terminal of a cell, a

positive-electrode can, a negative-electrode cap, etc. are made to serve a double purpose like the example shown in drawing 3 and drawing 4 , for example. In the example shown in drawing 3 , the positive-electrode can 406 and the negative-electrode cap 405 serve as cell housing which serves as an in-and-out force terminal, respectively in the example which the positive-electrode can 306 and the negative-electrode cap 305 show to drawing 4 . As an ingredient of cell housing which serves as an in-and-out force terminal, stainless steel is used suitably. Especially, a titanium clad stainless plate, a copper clad stainless plate, a nickel-plating steel plate, etc. are used abundantly.

[0088] Since the positive-electrode cans 306 and 406 serve as cell housing in the example shown especially in drawing 3 and drawing 4 , the above-mentioned stainless steel is desirable. On the other hand, when a positive-electrode can etc. does not make cell housing serve a double purpose, as the quality of the material of cell housing, the composite of plastics, such as metals, such as zinc, and polypropylene, a metal or a glass fiber, and plastics is used besides stainless steel.

[0089] (Relief valve) It is desirable as a safety practice when the internal pressure of a cell increases in the rechargeable battery of this invention that a relief valve (it is 414 at the example shown in drawing 4 ) is prepared. as a relief valve --- rubber, a spring, a metal ball, and a burst --- it can \*\*\*\*\* that it is \*\*\*\*.

[0090]

[Example] Hereafter, this invention is explained to a detail based on an example. In addition, this invention is not limited to these examples.

[0091] In example 1 this invention, the lithium secondary battery of a coin form like the cross-section structure shown in drawing 3 was produced. The negative electrode covered with the macromolecule-liquid crystal bipolar membrane for internal short circuit prevention by the dendritic growth of the lithium at the time of charge was used for the negative-electrode front face. Below, with reference to drawing 3 , the production procedure of each structure of a cell and the assembly of a cell are explained. In addition, all actuation was performed in argon gas.

[0092] (1) The metal lithium foil was stuck to the expanded metal of the production procedure \*\* copper of the negative-electrode (active material) layer 301 by pressure, and the negative-electrode layer 301 was produced.

[0093] (2) the product made from Merck which shows the covering \*\* polyvinyl chloride of the negative electrode in giant-molecule-liquid crystal bipolar membrane, and a negative dielectric anisotropy --- the



dichloroethane was added and the spreading solution was prepared, after mixing liquid crystal ZLI-4519 so that it may become the weight ratios 40/60.

[0094] \*\* The negative-electrode (active material) layer 301 of the metal lithium foil covered with the poly membrane 315 which impressed the magnetic field, dried perpendicularly to the metal lithium foil surface after applying the spreading solution prepared by the above-mentioned \*\*, ultraviolet rays were subsequently made to irradiate and construct a bridge over the metal lithium foil front face stuck to the expanded metal of the copper produced above (1) by pressure, and liquid crystal distributed was obtained.

[0095] (3) After mixing production procedure \*\* electrolytic manganese dioxide and the lithium carbonate of the positive-electrode (active material) layer 303 by the mole ratio of 1:0.4, it heat-treated at 800 degrees C, and the lithium-manganic acid ghost was prepared.

\*\* After mixing carbon powder 3wt(weight) % of acetylene black, and Pori fluoride kinky thread NIDEN powder 5wt% to the lithium-manganic acid ghost prepared in the above-mentioned \*\*, the N-methyl-2-pyrrolidone was added.

\*\* After carrying out spreading desiccation of the paste obtained by the above-mentioned \*\* at aluminium foil, reduced pressure drying was carried out at 150 degrees C, and the positive-electrode (active material) layer 303 was produced.

[0096] (4) production procedure [ of the electrolytic solution 307 ] \*\* -- the solvent which carried out equivalent mixing of the ethylene carbonate (EC) which fully removed moisture, and the dimethyl carbonate (DMC) was prepared.

\*\* What carried out 1M (mol/l) dissolution of the 4 fluoride [ lithium borate ] salt was used for the solvent obtained by the above-mentioned \*\* as the electrolytic solution.

[0097] (5) the fine hole of separator 307 polyethylene -- liquid retaining of the electrolytic solution adjusted by (4) using the separator was carried out.

[0098] (6) The separator 307 which carried out liquid retaining of the electrolytic solution was inserted between the negative-electrode layer 301 covered with the assembly \*\* poly membrane 315 of a cell, and the positive-electrode layer 303, and it inserted in the positive-electrode can 306 of the stainless steel material of a titanium clad. Furthermore, the above-mentioned electrolytic solution was poured in into the positive-electrode can 306, and liquid retaining of the electrolytic solution was carried out to the poly membrane 315.

\*\* The negative-electrode cap 305 of the stainless steel material of the gasket 310 of polypropylene and a titanium clad was put on the positive-electrode can 306 obtained by the above-mentioned \*\*, and the \*\*\*\*\* lithium secondary battery was produced.

[0099] (Evaluation of a cell property) Below, the performance evaluation of the produced cell is explained. The performance evaluation followed the energy density per [ which is obtained in a charge-and-discharge cycle trial ] unit volume of a cell, and a cycle life.

[0100] The conditions of a cycle trial made 1 cycle the cycle which serves as charge and discharge of big current density (1 time as many current as capacity/time amount), i.e., 1C, from the recess for 30 minutes so that the dendritic growth of a negative-electrode active material may tend to occur at the time of charge on the basis of the electric capacity calculated from positive active material. the charge and discharge test of a cell -- the Hokuto Denko make --- HJ-106M were used. In addition, the charge and discharge test was started from charge, cell capacity was made into the amount of discharge of 3 cycle eye, and the cycle life was made into the count of a cycle which was less than 60% of cell capacity.

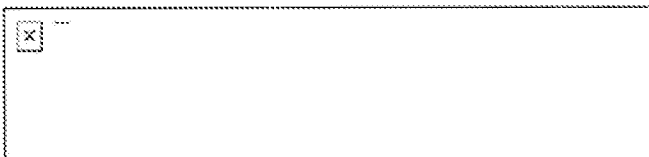
[0101] The value of [average (operating potential V) x discharge quantity of electricity (Ah)] / cell volume (l) estimated the energy density (Wh/l) per unit volume. In addition, about the cell volume, it calculated as volume of the appearance of the cel of a unit which consists of a negative electrode / a separator / a positive electrode. In the case of the lithium cell, the cut-off voltage of 4.5V and discharge was set as 2.5V for the cut-off voltage of charge.

[0102] Removing the point which uses the negative-electrode (active material) layer which did not cover macromolecule-liquid crystal bipolar membrane with the example of one example of a comparison as a negative electrode, except for not carrying out covering actuation of the macromolecule-liquid crystal bipolar membrane in an example 1, other points produced the cell like the example 1, and evaluated by this example similarly.

[0103] Table 1 summarizes the performance evaluation (cycle life) of the lithium secondary battery produced in the example 1 and the example 1 of a comparison. The \*\*\*\* evaluation result standardized the value of the example 1 of a comparison as 1.0 to this cycle life, and indicated the value of an example 1 to it.

[0104]

[Table 1]



[0105] Moreover, 10 cycle deed cell can was opened for the charge and discharge test on condition that the above about the cell independently produced in the example 1 and the example 1 of a comparison, and microscope observation of the condition of the dendritic growth in the anode of a cell was carried out. Although generating of a dendrite was not seen by the cell of an example 1, generating of a dendrite was observed in the example 1 of a comparison. Therefore, it turned out that there is no generating of a dendrite also in prolonged use in the rechargeable battery by which the negative-electrode top of an example 1 was covered by liquid crystal polymer bipolar membrane, and a long cycle life is acquired.

[0106] In the example of two examples, the lithium secondary battery of a coin form like the cross-section structure shown in drawing 3 was produced. Except for the point of having used for the negative electrode the aluminium foil covered with the liquid crystal polymer film, and having used the lithium-nickel oxide for positive active material, the rechargeable battery was produced like the example 1 except it.

[0107] Below, with reference to drawing 3, the production procedure of the negative electrode and positive electrode of a cell is explained.

(1) The front face was etched in 5% of the weight of the potassium-hydroxide water solution, the nitric-acid water solution neutralized the production procedure \*\* aluminium foil of a negative electrode, the hydrochloric-acid water solution was used for the electrolytic solution after rinsing, GURASHI carbon was used for the counterelectrode, and the aluminium foil which carried out electrolysis ENNGU of the aluminium foil which performed the above-mentioned processing, rinsed it, and raised surface area after reduced pressure drying was prepared. At the time of the charge in a cell, the lithium which is a negative-electrode active material will deposit on this aluminum front face, and a negative-electrode active material layer will be formed.

[0108] (2) Azobisisobutyronitril was added in the tetrahydrofuran solution which mixed 2 % of the weight of hoe lithium fluoride to the KORESU tick liquid crystal polymer of covering \*\* Pori (the 4 and 4'-diauxy 2, 2'-dimethyl azoxybenzene (+3)-methyl hexane JIOIRU) of the negative electrode in the liquid crystal polymer film, and the spreading solution was prepared.

\*\* The negative electrode of the aluminium foil which gave the spreading solution prepared by the above-mentioned \*\* by the spin coater, heat-treated at 100 degrees C under reduced pressure after spreading on the aluminium foil front face produced above (1), and was covered with the polymer liquid crystal film on it was prepared.

[0109] (3) After mixing the production procedure \*\* lithium nitrate and nickel carbonate of the positive-active-material layer 303 by the mole ratio of 1:1, it heat-treated in 750-degree-C air air current, and the lithium-nickel oxide was prepared.

\*\* After mixing carbon powder 3wt(weight) % of acetylene black, and Pori fluoride kinky thread NIDEN powder 5wt% to the lithium-nickel oxide prepared in the above-mentioned \*\*, the N-methyl-2-pyrrolidone was added.

\*\* After carrying out spreading desiccation of the paste obtained by the above-mentioned \*\* at aluminium foil, reduced pressure drying was carried out at 150 degrees C, and the positive-active-material layer 303 was produced. Other points produced the cell like the example 1.

[0110] Removing the point which used what did not cover the polymer liquid crystal film with the example of two examples of a comparison as a negative electrode, except for not carrying out covering actuation of the polymer liquid crystal film in an example 2, other points produced the cell like the example 2, and evaluated by this example similarly.

[0111] Table 2 summarizes the performance evaluation (cycle life) of the lithium secondary battery produced in the example 2 and the example 2 of a comparison. The \*\*\*\* evaluation result standardized the value of the example 2 of a comparison as 1.0 to this cycle life, and indicated the value of an example 2 to it.

[0112]

[Table 2]


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Therefore, in the rechargeable battery by which the negative electrode of an example 2 was covered by the polymer liquid crystal film, it turned out that a cycle life becomes long.

[0113] In the example of three examples, the lithium secondary battery of a coin form like the cross-section structure shown in drawing 3 was produced. In a negative electrode, a graphite is differed [ oxide / lithium-cobalt ] in an example 1 in that the polymer gel film was prepared between the negative electrode and the positive electrode at

positive active material as intercalation matter which stores a lithium between layers at the time of charge. The rechargeable battery was produced like the example 1 except it.

[0114] Below, with reference to drawing 3, the production procedure of the negative electrode and positive electrode of a cell is explained.

(1) After dipping the microporous polypropylene film which performed hydrophilic processing in the water solution of the N and N-diethyl acrylamide which is the monomer of a polymer and acrylic-acid sodium which formed the production procedure \*\* nitrogen gas of the polymer gel film into sink deoxidation and irradiating a gamma ray, water washed, reduced pressure drying of the unreacted monomer was removed and carried out, and the microporous polypropylene film with polymer gel was obtained.

[0115] (2) After mixing polyvinylidene fluoride powder 5wt% to the impalpable powder of the natural graphite heat-treated at 2000 degrees C among the production procedure \*\* argon gas air current of a negative electrode, the N-methyl-2-pyrrolidone was added and the paste was prepared.

\*\* After carrying out spreading desiccation of the paste obtained by the above-mentioned \*\* at copper foil, reduced pressure drying was carried out at 150 degrees C, and the negative electrode was produced. A lithium will intercalate in this graphite and the negative-electrode (active material) layer 301 will be formed at the time of charge.

[0116] (3) After mixing the production procedure \*\* lithium carbonate and cobalt carbonate of the positive-electrode (active material) layer 303 by the mole ratio of 1:2, it heat-treated by 800-degree-C air air current, and the lithium-cobalt oxide was prepared.

\*\* After mixing carbon powder 3wt(weight) % of acetylene black, and Pori fluoride kinky thread NIDEN powder 5wt% to the lithium-cobalt oxide prepared in the above-mentioned \*\*, the N-methyl-2-pyrrolidone was added.

\*\* After carrying out spreading desiccation, reduced pressure drying of the paste obtained by the above-mentioned \*\* was carried out to the charge collector which is expanded metal-like aluminium foil at 150 degrees C, and the positive-active-material layer 303 was produced.

[0117] (4) Between the assembly \*\* positive electrode of a cell, and the negative electrode, the microporous polypropylene film with polymer gel (the electrolytic solution is the same as an example 1) to which it produced by (1) and liquid retaining of the electrolytic solution was carried out was inserted, the laminated structure of the positive electrode 102 as shown in drawing 2 (c), the poly membrane 100 which carried out liquid retaining of the electrolytic solution, and a

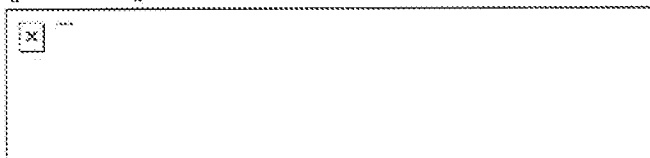
negative electrode 101 was formed, and it inserted in the positive-electrode can 306 of the stainless steel material of a titanium clad.  
[0118] \*\* The negative-electrode cap 305 of the stainless steel material of the gasket 310 of polypropylene and a titanium clad was put on the positive-electrode can 306 obtained by the above-mentioned \*\*, and the \*\*\*\*\* lithium secondary battery was produced. That is, the poly membrane 315 is equipped with the function in the separator 307 and this layer by the structure shown in drawing 3 . The engine performance was evaluated like [ rechargeable battery / which was obtained ] the example 1.

[0119] In the example of three examples of a comparison, other points produced the rechargeable battery like the example 3 except for the point which does not use the polymer gel film between a positive electrode and a negative electrode. That is, the microporous polypropylene film was used as a separator.

[0120] Table 3 summarizes the performance evaluation (cycle life) of the lithium secondary battery produced in the example 3 and the example 3 of a comparison. The \*\*\*\* evaluation result standardized the value of the example 3 of a comparison as 1.0 to this cycle life, and indicated the value of an example 3 to it.

[0121]

[Table 3]



Therefore, in the lithium secondary battery with which the polymer gel film was fastened between the positive electrode of an example 3, and the negative electrode, it turned out that a cycle life improves.

[0122] In addition, when the energy density per unit volume of the rechargeable battery of an example 1, an example 2, and an example 3 was standardized having used energy density per unit volume of the rechargeable battery of the example 3 of a comparison as 1.0, it was 1.9, 1.6, and 1.0, respectively. The comparison of this energy density showed that a cycle life was all long and a rechargeable battery with a still higher energy density was obtained in the lithium secondary battery of examples 1-3.

[0123] In the examples 1-3, lithium-cobalt oxide, the lithium-nickel oxide, and the lithium-manganic acid ghost were used as positive active material in a lithium secondary battery. However, it is not limited to

this and various kinds of positive active material, such as a lithium-banazin san ghost and a lithium-ferric acid ghost, can also be adopted. Moreover, a graphite, aluminum, and a metal lithium were used as a negative-electrode ingredient. However, it is not limited to this and the various carbon materials which calcinate organic resin and are obtained, a transition-metals oxide, a transition-metals sulfide, etc. can be adopted.

[0124] Moreover, although one kind of thing was used to examples 1-3 also about the electrolytic solution, this invention is not limited to this.

[0125] In the example of four examples, the nickel-zinc rechargeable battery of a coin form like the cross-section structure shown in drawing 3 was produced.

[0126] Below, with reference to drawing 3, the production procedure of each structure of a cell and the assembly of a cell are explained.

(1) Pass and deoxidation-ize nitrogen gas after dissolving the acrylamide which is the monomer of the production procedure \*\* polymer of the polymer gel film 315, and TORIMECHIRU (N-acryloyl-3-aminopropyl) ammonium iodide and the N,N'-methylenebis acrylamide of a cross linking agent in water. After dipping the microporous polypropylene film which performed hydrophilic processing, adding the ammonium persulfate and tetramethylethylenediamine of a polymerization initiator in this liquid, making it react to it about 30 minutes and obtaining gel, It washed with water, reduced pressure drying of the unreacted monomer was removed and carried out, and the microporous polypropylene film with polymer gel was obtained.

[0127] (2) The \*\*\*\*\* (matter) layer 301 was obtained by adding and kneading water, making it the shape of a paste, plastering the punching metal plate of a nickel metal and carrying out press forming to both sides of the punching metal of the production procedure \*\* copper of the negative-electrode (active material) layer 301 after desiccation by using polyvinyl alcohol as a binder, at the mixture of zinc powder and zinc oxide powder.

[0128] (3) the production procedure \*\* nickel hydroxide of the positive-electrode (active material) layer 303 --- nickel powder --- in addition --- as a binder --- a carboxymethyl cellulose and water --- in addition, it dried, pressed and produced, after preparing the paste and filling up the foam (the Sumitomo Electric Industries make, a cel helmet) of nickel.

[0129] (4) The 30wt% potassium-hydroxide water solution which added the production procedure \*\* lithium hydroxide of the electrolytic solution 307 was used.

(5) The thing of 100-micrometer thickness which sandwiched the polypropylene nonwoven fabric which carried out separator 307\*\* hydrophilic processing with the microporous polypropylene film which carried out hydrophilic processing was used.

[0130] (6) Between the assembly \*\* negative-electrode (active material) layer 301 of a cell, and the positive-electrode (active material) layer 303, like the laminated structure of the positive electrode 102 shown in drawing 2 (a), a separator and the electrolytic solution 103, a poly membrane 100, and a negative electrode 101, the separator 307 which carried out liquid retaining of the electrolytic solution which mentioned above the microporous polypropylene film with polymer gel produced above (1) to the negative-electrode side to the positive-electrode side was inserted, and it inserted in the positive-electrode can 306 of the stainless steel material of a titanium clad. Furthermore, the electrolytic solution was poured in into the positive-electrode can 306, and the electrolytic solution was made to hold to a poly membrane 315.

[0131] \*\* The negative-electrode cap 305 of the stainless steel material of the gasket 310 of polypropylene and a titanium clad was put on the positive-electrode can 306 obtained by the above-mentioned \*\*, and the \*\*\*\*\* nickel-zinc rechargeable battery was produced.

[0132] Below, the performance evaluation of the produced nickel-zinc cell is explained. The performance evaluation followed the cycle life acquired in a charge-and-discharge cycle trial.

[0133] The conditions of a cycle trial made 1 cycle the cycle which serves as charge and discharge of 1C (1 time as many current as capacity/time amount) from the recess for 30 minutes on the basis of the electric capacity calculated from positive active material. the charge and discharge test of a cell -- the Hokuto Denko make -- HJ-106M were used. In addition, the charge and discharge test was started from charge, cell capacity was made into the amount of discharge of 3 cycle eye, and the cycle life was made into the count of a cycle which was less than 60% of cell capacity. In the case of the nickel-zinc cell, the cut-off voltage of 2.0V and discharge was set as 0.9V for the cut-off voltage of charge.

[0134] In the example of four examples of a comparison, except for the point which did not use the polymer gel film, other points produced the nickel-zinc rechargeable battery like the example 4, and performed the performance evaluation similarly.

[0135] Table 4 summarizes the performance evaluation (cycle life) of the nickel-zinc rechargeable battery produced in the example 4 and the



example 4 of a comparison. The \*\*\*\* evaluation result standardized the value of the example 4 of a comparison as 1.0 to this cycle life, and indicated the value of an example 4 to it.

[0136]

[Table 4]

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Therefore, in the nickel-zinc rechargeable battery which fastened the polymer gel film between the positive electrode of an example 4, and the negative electrode, it turned out that a longer cycle life is acquired.

[0137] In the example of five examples, the air zinc rechargeable battery of a coin form like the cross-section structure shown in drawing 3 was produced.

[0138] Below, with reference to drawing 3, the production procedure of each structure of a cell and the assembly of a cell are explained.

(1) the product made from Merck which shows the production procedure \*\* polyvinyl chloride of the giant-molecule-liquid crystal bipolar membrane 315, and a negative dielectric anisotropy --- after mixing liquid crystal ZLI-2806 so that it may become the weight ratios 40/60, the giant-molecule-liquid crystal bipolar membrane 315 was obtained after applying the solution which dissolved by the dichloroethane to the microporous polypropylene film which applied the ethanol solution of lecithin beforehand and was dried and by which hydrophilic processing was carried out.

[0139] (2) The negative-electrode (active material) layer 301 was obtained by applying the paste which added, kneaded and prepared polyvinyl alcohol and water to the mixture of zinc powder and zinc oxide powder to both sides of the punching metal of the production procedure \*\* copper of the negative-electrode (active material) layer 301, and carrying out a desiccation press.

[0140] (3) A manganese dioxide, nickel oxide, cobalt oxide, and tetrafluoroethylene polymer powder were mixed to the production procedure \*\* acetylene black of a positive electrode, and what applied to the copper mesh which carried out nickel plating of what added and pasted the sault PAKO nak (Nippon Oil & Fats Co., Ltd. make, fine-particles fluororesin coating) 5wt% xylene solution, and was fabricated at 170 degrees C through the pressurization heater roller after hardening was used as the positive electrode. In this positive electrode,

air will diffuse at the time of discharge, and the oxygen of an active material will react.

[0141] (4) The 30wt% potassium-hydroxide water solution which added the production procedure \*\* lithium hydroxide of the electrolytic solution 307 was used.

(5) The thing of 100-micrometer thickness which sandwiched the polypropylene nonwoven fabric which carried out separator 307\*\* hydrophilic processing with the microporous polypropylene film which carried out hydrophilic processing was used.

[0142] (6) Between the assembly \*\* negative-electrode (active material) layer 301 of a cell, and the positive-electrode (active material) layer 303 The positive electrode 102 shown in drawing 2 (a), a separator and the electrolytic solution 103, a poly membrane 100, and the microporous polypropylene film with macromolecule-liquid crystal bipolar membrane produced above (1) to the negative-electrode side like the laminated structure of a negative electrode 101 The separator 307 which carried out liquid retaining of the electrolytic solution to the positive-electrode side was inserted, and it inserted in the positive-electrode can 306 with an air incorporation hole of the stainless steel material of the titanium clad which inserted the polytetrafluoroethylene film of air diffusion paper and the water-repellent film previously. Furthermore, the electrolytic solution was poured in into the positive-electrode can 306, and the electrolytic solution was made to hold on a polypropylene film.

[0143] \*\* The negative-electrode cap 305 of the stainless steel material of the insulating backing 310 of polypropylene and a titanium clad was put on the positive-electrode can 306 obtained by the above-mentioned \*\*, and the caulking \*\*\*\*\* zinc rechargeable battery was produced.

[0144] In the example of five examples of a comparison, other points produced the air zinc rechargeable battery like the example 5 except for the point which did not use macromolecule-liquid crystal bipolar membrane in the positive electrode and the negative electrode.

[0145] The performance evaluation of the cell produced in the example 5 and the example 5 of a comparison was performed on the same conditions as the nickel-zinc cell of an example 4.

[0146] Table 5 summarizes the performance evaluation of the air-zinc rechargeable battery produced in the example 5 and the example 5 of a comparison. The \*\*\*\* evaluation result standardized the value of the example 5 of a comparison as 1.0 to this cycle life, and indicated the value of an example 5 to it.

[0147]

[Table 5]

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Therefore, by adopting the air-zinc rechargeable battery which fastened polymer liquid crystal bipolar membrane between the positive electrode of an example 5 and the negative electrode showed that a rechargeable battery with the more excellent long cycle life was obtained.

[0148]

[Effect of the Invention] As explained above, according to this invention, especially a negative-electrode active material is generated in a negative electrode in the rechargeable battery which is a lithium or zinc at the time of charge, and growth of the dendrite leading to performance degradation can be controlled. Consequently, production of a lithium secondary battery and a nickel zinc rechargeable battery with a high energy density with a long and cycle life, an air zinc rechargeable battery, etc. is attained.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the cross-section block diagram showing an example of the rechargeable battery of this invention.

[Drawing 2] It is the conceptual diagram showing the example of arrangement of the poly membrane which are the negative electrode in the rechargeable battery of this invention, a positive electrode, a separator, and a means to prevent the dendritic growth of a negative-electrode active material.

[Drawing 3] It is the sectional view showing an example of the monolayer type flat form cell of this invention.

[Drawing 4] It is the sectional view showing an example of the spiral type cylindrical cell of this invention.

[Drawing 5] It is a conceptual diagram explaining the function of the rechargeable battery of this invention.

[Description of Notations]

100 Poly Membrane for Short Circuit Prevention

101 Negative Electrode

102 Positive Electrode  
103 Separator and Electrolytic Solution  
104 Battery Case (Cell Housing)  
105 Negative-Electrode Terminal  
106 Positive-Electrode Terminal  
107 Electric-Field Concentration Section  
108 Part Which Poly Membrane for Short Circuit Prevention Formed into  
High Resistance  
109 Power Source for Charge  
301 Negative-Electrode Layer  
401 Negative-Electrode (Active Material) Layer  
303 Positive-Electrode Layer  
403 Positive-Electrode (Active Material) Layer  
305,405 Negative-electrode cap (negative-electrode terminal)  
306,406 Positive-electrode can (positive-electrode terminal)  
307,407 Separator holding the electrolytic solution  
310,410 Gasket  
400 Negative-Electrode Charge Collector  
402 Negative Electrode  
404 Positive-Electrode Charge Collector  
408 Positive Electrode  
411 Electric Insulating Plate  
412 Negative-Electrode Lead  
413 Positive-Electrode Lead  
414 Relief Valve  
315,415 Poly membrane for short circuit prevention

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